on the gelatin strands. The mechanism of the charge transfer under such conditions remains, however, unclear. The structure proposed by Petit et al. is close to a model postulated previously by the present authors (ref 2) and is likely to appear at high amounts of gelatin and low amounts of the polar phase. Less typical structures may, however, be expected if the volume fraction of water is increased at constant surfactant and gelatin concentrations. In particular, we do not think that many gelatin molecules will be present in the apolar phase if enough water is available for the solubilization of their polar side groups.

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Nonequilibrium Processes In Polymers Undergoing Interchange Reactions. 2. Reaction–Diffusion Processes

John A. Pojman,*

Department of Chemistry and Biochemistry, University of Southern Mississippi, Southern Station, Box 5043, Hattiesburg, Mississippi 39406-5043

Alejandro L. Garcia,

Department of Physics, San Jose State University, San Jose, California 95192

Dilip K. Kondepudi,

Department of Chemistry, Box 7486, Wake Forest University, Winston-Salem, North Carolina 27109

and Christian Van den Broeck

Limburgs Universitair Centrum, B-3610 Diepenbeek, Belgium (Received: November 19, 1990)

A reaction–diffusion system of polymers undergoing interchange reactions is studied. The equation that describes the dynamics of the system is similar to the Boltzmann equation for a gas of hard spheres. We consider a one-dimensional system in which the average length and the concentrations at the boundaries are fixed. The resulting steady states are obtained analytically and with numerical integration of equations obtained by using a local equilibrium approximation. Monte Carlo simulations of experimentally realizable conditions were performed and compared. The results reveal a nonlinear distribution of molecular concentration and mass. The entropy of the polymer distributions is calculated as function of position and shown to be less than the entropy for the distributions without interchange reactions. The diffusion of a square pulse is also considered.

Introduction

This is the second in a series of theoretical studies on nonequilibrium processes in condensation polymers undergoing interchange reactions. Interchange reactions occur among polyesters and polyamides when two molecules exchange segments of their length. Polyester interchange reactions are often called transesterifications. The dominant reaction among polyesters in solution is the acid-catalyzed attack of a hydroxyl end of one polymer upon the ester linkage of another polymer molecule. This reaction, called alcoholysis, is shown in Figure 1. Direct esterester interchange is more important with high polymers in the melt. While the number of molecules is unchanged by interchange reactions, the molecular weights distribution is affected. Flory was the first to consider this effect and to show that the rate of reaction is approximately independent of the position of the ester linkage within the molecule, or the length of the molecule.

Interchange reactions are used industrially with applications ranging from altering the melting point of fats and oils to preparing heterogeneous block polymers from a mixture of two different homogeneous polymers. They also can affect the blending of homopolymer mixtures. There have been several reviews of the applications, techniques, and chemistry of these reactions. Earlier works, the close mathematical analogy between interchange reactions and collisions in a gas of hard spheres was noted. The equations of the polymer system are similar in mathematical structure to the well-known Boltzmann equation for the gas of hard spheres. This analogy is useful because it enables us to think about the collisions involving interchange reactions in a similar way as we look at processes in the hard-sphere gas. For example, from the Boltzmann equation, which is a nonlinear integral equation, one can obtain the so-called "hydrodynamic equations" which are a set of closed equations for the averages of quantities such as energy and density. In an unstirred system, we can do the same in the case of polymers undergoing interchange reactions and diffusion and can obtain a set of closed equations for the concentration and average length as a function of position.

Using these equations we can study a process similar to heat conduction in a gas of hard spheres. In this approach, the average length of the polymers corresponds to the average energy of a gas molecule. In a gas, molecules move from one point to another through rectilinear motion with their velocities changing via


(3) Flory, P. J. Am. Chem. Soc. 1942, 64, 1205.


via interchange reactions.

collisions. The corresponding processes in polymers are the
diffusion motion of polymers and the changing of their lengths
change reactions is described in terms of the following equation:

rotations of either reaction are the same. For species longer
than trimers, the product distribution depends upon which bond the
hydroxyl attacks.

The friction constant, \( \gamma \), is useful because it provides the limiting behavior.

We present the theoretical derivation of the equations that
describe a reaction-diffusion process, obtain the approximate
solutions of these equations, and compare them with the results
of numerical simulations with chemically realistic parameters for
open and fixed boundary problems. The steady-state distribution of
polymers is not those predicted by Fick's law. We investigate
how interchange reactions increase the diffusive particle flux, and
discuss insights into its origins.

Reaction–Diffusion Equation

For mathematical convenience, we identify polymers by the
number of bonds rather than the number of monomer units they
contain. (The number of bonds in a polymer is one less than the
length of the polymer.) The polymer system undergoing inter-
change reactions is described in terms of the following equation:

\[
\frac{\partial f(n,r,t)}{\partial t} = D(n) \nabla^2 f(n,r,t) + C_l(f(n,r,t))
\]  

(1)

Here \( f(n,r,t) \) is the concentration of polymers with \( n \) bonds at the
position \( r \) at time \( t \). \( D(n) \) is the diffusion coefficient, and \( C_l(f(n,r,t)) \)
represents the rate of change of \( f(n,r,t) \) due to interchange re-
actions. The explicit form of \( C_l \) (derived in ref 9) is

\[
C_l(f) = \sum_{n_1,n_2} \sum_{n_3} \sigma(n_1,n_2,n_3) (f(n_1,n_3) f(n_2,n_3) - f(n_1,n_2) f(n_2,n_3))
\]  

(2)

where \( \sigma(n_1,n_2,n_3) \) is the rate constant for the reaction in which
a polymer with \( n_1 \) bonds reacts with a polymer with \( n_2 \) bonds to
produce two polymers with \( n_1 \) and \( n_3 \) bonds. The term \( C_l(f(n,r,t)) \)
corresponds to the collision operator in the Boltzmann equation.

The length dependence of a polymer diffusion coefficient has
been obtained by Kirkwood and Riseman for a flexible molecule
on the basis of the random coil model with hindered internal
rotation and of inhibited flow through the coil and recently
discussed by Stepto.

\[
D(n) = \left[ 1 + \left( 8 \lambda_0 / 3 \right) (n + 1)^{1/2} \right] \frac{kT}{\eta b^2}
\]  

(3)

In the limit of long polymers, \( D(n) \) is proportional to \( \eta b L \) where \( L \) is the friction constant, \( \gamma \), is characteristic of the solvent and the
monomer, and \( \lambda_0 \) is a characteristic length between segments.

This model does not directly apply to polyesters, it is a useful starting point for demonstrating that interchange reactions

can have interesting effects on real systems. We assume that the
diffusion coefficient is independent of concentration.

Reaction Invariants and Analogues of Hydrodynamic
Equations

The interchange reaction has two invariants similar to the
collisional invariants in a hard-sphere gas. In an interchange
reaction, neither the number of bonds nor the number of molecules
changes. Hence, we have the conservation of the number of
molecules and the conservation of the total number of bonds. The
conservation of the total number of molecules implies that the
sum of the terms, \( C_e(n) \), describing the rate of change of the concentration of polymers with \( n \) bonds must sum to zero because
processes producing molecules with \( n \) bonds must be exactly balanced by processes consuming molecules with \( n \) bonds:

\[
\sum_{n=0}^{\infty} C_e(n) = 0
\]

Similarly, because the total number of bonds remains invariant
we have

\[
\sum_{n=0}^{\infty} n C_e(n) = 0
\]

In the case of a gas, a set of equations reduced in the number of
independent variables, called the hydrodynamic equations, can
be derived for the particle number density and the average energy.
Each variable in the hydrodynamic equations corresponds to a
conserved quantity. We do the same for the polymers and define
a total molecular concentration by

\[
N(r,t) = \sum_{n=0}^{\infty} f(n,r,t)
\]

and the average bond number, \( \bar{n}(r,t) \), by

\[
\bar{n}(r,t) = \frac{1}{N(r,t)} \sum_{n=0}^{\infty} n f(n,r,t)
\]

\[
N(r,t) = \sum_{n=0}^{\infty} f(n,r,t)
\]

and the average bond number, \( \bar{n}(r,t) \), by

\[
\bar{n}(r,t) = \frac{1}{N(r,t)} \sum_{n=0}^{\infty} n f(n,r,t)
\]

(6)

Even though the reaction term \( C_l(f) \) does not appear in the above
two equations, it must be noted that eqs 8 and 9 are not closed
in variables \( N \) and \( \bar{n} \); interchange reactions play a role in deter-
mining the form of the concentrations \( f(n,r,t) \).

The reaction rate \( C_l(f) \) of hydrodynamic equations—we use the assumption of local equilibrium. This is
the assumption that the interchange rate is sufficiently large to
maintain a local equilibrium for the distribution of polymer length;
that is, in each infinitesimally small region of the solution, dr, the
collection distribution, \( f(n,r,t) \), is very close to a Flory distri-
bution. The Flory distribution depends on \( N \) and \( \bar{n} \), both of
which may vary with position.

The Flory equilibrium distribution \( f_0 \) defined as the solution of
\( C_l[f] = 0 \), can be obtained from eq 2.9 It has the following
general form, analogous to the Maxwell–Boltzmann distribution:

\[
f_0(n,r) = N(1 - e^{-\beta}) e^{\beta n}
\]

(10)

Here \( \beta = \beta(r,t) \) is a function of the position \( r \) and time \( t \); it is

related to the average bond number \( \rho(x,t) \) as follows:

\[
\beta = -\ln \left( \rho / (N + 1) \right)
\]

(In Flory's notation \( \exp(-\beta) = \rho \), the extent of polymerization).

The Flory distribution is the equilibrium distribution for interchange reactions in the same way as the Maxwell-Boltzmann distribution is the equilibrium distribution for a dilute gas. Reaction equilibrium does not specify the values of \( N \) and \( \rho \) but the two quantities are invariant during the interchange reaction. Both \( N \) and \( \rho \) are functions of position and time.

With the assumption of local Flory equilibrium, we may now use eq \( 10 \) for \( f \) in eqs \( 8 \) and \( 9 \):

\[
\frac{\partial N(x,t)}{\partial t} = \nabla^2 \left[ (N(1 - e^\beta)) \left( \sum_{n=0}^{\infty} D(n) e^{\beta n} \right) \right]
\]

\[
\frac{\partial}{\partial t} \left[ N(r,t) \rho(r,t) \right] = \nabla^2 \left[ (N(1 - e^\beta)) \left( \sum_{n=0}^{\infty} n D(n) e^{\beta n} \right) \right]
\]

We now have a set of closed equations for the variables \( N \) and \( \rho \). These nonlinear equations are the analogues of the hydrodynamic equations of a gas.

Though closed and containing just two variables, eqs \( 12 \) and \( 13 \) are very complicated and highly nonlinear. They can be considerably simplified in the case of the average bond number, \( \rho \), being greater than 10. For this case, the diffusion coefficient, eq \( 3 \), can be approximated by \( D(n) = D_0(n + 1)^{-\gamma} \), where \( D_0 \) is the monomer diffusion coefficient. We substitute this form of \( D(n) \) into eqs \( 12 \) and \( 13 \) and convert the summations into integrals.\(^{14}\)

\[
\sum_{n=0}^{\infty} n e^{\beta n} \approx (\pi \rho)^{1/2}
\]

\[
\sum_{n=0}^{\infty} n e^{\beta n} \approx \frac{1}{2} (\pi \rho)^{1/2}
\]

Substituting eqs \( 14 \) and \( 15 \) into eqs \( 12 \) and \( 13 \), we obtain the analogues of the hydrodynamic equations for polymers:

\[
\frac{\partial N}{\partial t} = \nabla^2 \left( D^*(\rho) N \right)
\]

\[
\frac{\partial}{\partial t} \left[ N(r,t) \rho(r,t) \right] = \nabla^2 \left( D^*(\rho) N \right)
\]

where

\[
D^*(\rho) = D_0 (\pi / \rho)^{1/2}
\]

In the following sections we will discuss the use and limitations of the equations by comparison to numerical simulations.

**Transport between Reservoirs**

We examine the following one-dimensional system (schematically illustrated in Figure 2): A straight tube connects two large reservoirs containing polymer solutions with molecular concentrations \( N(0) \) and \( N(L) \), and average bond numbers \( \rho(0) \) and \( \rho(L) \). The ends of the tube are at \( x = 0 \) and \( x = L \). The system relaxes to a steady state with a constant flow of molecules and mass.

Some properties of the steady state can be obtained from eqs \( 8 \) and \( 9 \) without any approximations. To begin with, because both \( N \) and \( \rho \) are time independent, we have

\[
\frac{\partial^2}{\partial x^2} \left( \sum_{n=0}^{\infty} D(n) f(n,x) \right) = 0
\]

\[
\frac{\partial^2}{\partial x^2} \left( \sum_{n=0}^{\infty} n D(n) f(n,x) \right) = 0
\]

This implies that the sum \( \sum_{n=0}^{\infty} D(n) f(n,x) \) and \( \sum_{n=0}^{\infty} n D(n) f(n,x) \) are linear functions of \( x \).

Let us consider two limiting cases for the length dependence of the diffusion coefficient in order to obtain some simple analytical results which apply to either very short polymers or to long ones.

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\(^{14}\) Abramowitz, M.; Stegun, I. Handbook of Mathematical Functions; Dover: New York, 1972.
Note that both eqs 29 and 30 are nonlinear functions of position.

### Numerical Simulations

To solve eq 1 by standard finite difference methods is impractical as the reaction term, $C[J]$, is very complicated and highly nonlinear. We thus adopted a Monte Carlo approach. In a previous work\(^2\) we used a one-particle distribution function, $f(n,r,t)$, in the simulation of the interchange reactions. This approach was also applied for the reaction–diffusion case by treating diffusion as a one-dimensional random hop and decoupling it from the interchanges occurring in discrete bins. A description of this approach is provided in the Appendix. We also employed an algorithm which, instead of using the one-particle distribution function $f(n,r,t)$, uses the equivalent phase space representation: $[n,r]$, where $n$ is the number of bonds in the $i$th polymer and $r$ is its position. The algorithm was adapted from the direct simulation Monte Carlo (DSMC) method introduced by Bird.\(^5\) A detailed discussion of the simulation procedure has appeared elsewhere.\(^6\) Because both simulation approaches provided nearly identical results, we only present those from the one-particle distribution method.

We used the following values for the parameters in eq 2 by assuming the experiments were performed in benzene at 80 °C (conditions under which interchange reactions have been observed):\(^17\) $\lambda_0 = 0.5$ (ref 12); $b$ (distance between units in a polyester)\(^18\) $= 10^{-7}$ cm; $\eta =$ viscosity of benzene \(^9\) at 80 °C = 0.0033 g (cm·s)$^{-1}$ to obtain

$$D(n) = \frac{1 + 2.1(n + 1)^{1/2}}{n + 1} \times (1.3 \times 10^{-5}) \text{ cm}^2 \text{ s}^{-1}$$

This provides a monomer diffusion coefficient of $D_0 = 4 \times 10^{-5}$ cm\(^2\) s\(^{-1}\), which is a realistic value for a small organic molecule.\(^19\) Equation 31 was used throughout all the simulations.

The interchange reaction rate constant is defined by the following expression:

$$k = \frac{2k_{\text{inter}}[\text{polymer molecules}]}{\text{unit time-unit volume}}$$

The dependence of the interchange rate upon the average number of bonds has been considered in reference 9. Because no measurement of such a value has been made for interchange reactions in solution,\(^3\) we must estimate a value on the basis of work done on esterification reactions in solution. The interchange rate constant is of the same order of magnitude as that for esterification under the same conditions.\(^3\) From the work of Whitesell and Pojman,\(^21\) we estimate a rate constant of $10^{-3}$ (M·s)$^{-1}$.

### Simulation Results

#### Open System

The first physically realizable configuration we considered was that of a step distribution of polymers allowed to diffuse while undergoing interchange reactions. In the limiting case of local equilibrium, no significant effect on the molecular or mass distribution was observed.

#### Bounded System

The case when $n(0) = n(L)$, $N(0) \neq N(L)$ (equal polymer lengths, unequal concentrations) is not very interesting because the solution (eq 26) reduces to

$$N(x) = N(0) + (N(0) - N(0))x/L$$

$$n(x) = n(0) + (n(0) - n(0))L$$

In other words, the molecular concentration profile is linear and the average bond number is constant, as expected from Fick’s law.

On the other hand, the case $n(0) \neq n(L)$, $N(0) = N(L)$ presents some unusual results. Consider the initial condition:

$$N(0) = N(L) = 0.1 \text{ M}; \ n(0) = 1; \ n(L) = 19; \ L = 1 \text{ cm}$$

The solutions of eqs 12 and 13 and the simulation results are presented in Figure 3. Surprisingly, we see that the molecular concentration rises significantly in the center of the system, in Figure 3a; eq 29 indicates that it has a maximum at the center of the tube, $x = L/2$. Figure 3b shows $n$ as function of position, and Figure 3c shows the mass (the product of $n(x) + 1$) and $N(x)$ distribution versus position. Figure 3d demonstrates that if $D(n)$ is proportional to $(n + 1)^{-1}$, the molecular concentration is the same as without any interchange reaction, as predicted by eq 26.

The qualitative forms of $N(x)$ and $n(x)$ are correctly predicted by the analytical solutions in eqs 29 and 30, but the quantitative agreement is poor. However, the mass distribution is quite close to that obtained by numerical integration.

### Discussion

The central assumption in the formulation of the macroscopic equations is that the Flory distribution (eq 10) is always maintained locally. This assumption is certainly violated because the interchange reaction rate is low. To quantify this, we follow a procedure in gas dynamics and introduce the “polymer Knudsen number”:\(^22\)

$$K_n = \text{mean free path between interchange reactions/characteristic length scale}$$

The characteristic length for the steady-state problem is the length of the tube. When the Knudsen number is below $10^{-2}$, we say that the system is “reaction dominated” and can assume that the Flory distribution is maintained locally. However, if $K_n > 0.1$ then this assumption is no longer valid, and our hydrodynamic theory may break down. When the Knudsen number is very high, we may treat the system as “reactionless”. In some cases, eqs 12 and 13 or 19 and 20 will give acceptable results even for relatively large Knudsen numbers.

We calculate the time between interchange reactions for our system, $\tau$,

$$\tau = \frac{2k_{\text{inter}}[P]}{D}$$

where $[P]$ is the total molecular concentration. The mean free path of an average polymer molecule in this time is

$$d = \sqrt{\frac{D_{\text{tot}} \tau}{\tau}}$$

For $n$, we use the average of the two boundary values, 10, and substitute into eq 35 to calculate a $K_n \approx 0.07$. From the results of the simulations, we see that the assumption of local equilibrium allows the calculation of concentration distribution with good accuracy to that obtained by simulation.


\(^{(22)}\) In gas dynamics the Knudsen number is the ratio of the mean free path between collisions to the characteristic length (see ref 15).
Formation of Nonlinear Concentration Distribution. At the boundaries, interchange reactions between long and short polymers deplete the concentrations of those species and increase the concentrations of intermediate length molecules. In both reservoirs, short molecules outnumber long ones, because of the exponential nature of the length distribution. The short molecules will be replaced by diffusion from the reservoir faster than the long molecules, and faster than the intermediate ones can diffuse into the reservoir. (The form of the length dependence of the diffusion coefficient is important.) The net result is an increase in the molecular concentration and a decrease in the average number of bonds. The process will occur along the length of the tube until a steady state is reached.

Proposed Experimental Procedure. The molecular concentration distribution is independent of the rate of interchange, if that rate is larger enough to ensure that the mean free path between reaction is less than the system length. The distribution does depend on the form of the length dependence of the diffusion coefficient. Comparing our results with experiment would provide a test of the Kirkwood–Riseman theory of the diffusion coefficient. Using a variety of polymer systems would also provide information on the relationship between polymer structure and the length dependence of the diffusion coefficient.

Two methods could be used to confirm these predictions: Measuring the refractive index as a function of position along the reaction zone would provide the approximate polymer mass concentration. Spatially resolved measurements would be difficult to perform. However, if each polymer unit contains the same UV absorbing group, then UV absorbance can be an extremely accurate measure of polymer length. Using a diode array could provide spatially resolved data of the length (mass) distribution. This approach would also provide time resolved data as the system relaxes to the steady state.

Although the simulations do not directly apply to high polymers in the melt, the nonlinear mass profile should be observable when two polyester materials of different average length are placed in contact at high temperature. The direct ester–ester interchange coupled with diffusion may be the process causing "chemical healing" at the interface of two polyester materials.

Steady-State Thermodynamics. The conservation of bonds means that the enthalpy of the system does not change. The entropy is affected by the change in distributions brought about by interchange reactions. We can calculate the molar entropy of any distribution using Boltzmann's expression,

$$ S(x) = - k_B \sum_{n=0}^{\infty} f(n,x) N(x) \ln \left( \frac{f(n,x)}{N(x)} \right) $$

If we have an equilibrium, Flory distribution given by eq 10, we can derive an exact solution by substituting it into eq 37 and using the relations

$$ \sum_{n=0}^{\infty} e^{-\beta n} = S + 1; \quad \sum_{n=0}^{\infty} ne^{-\beta n} = n(n + 1) $$

to obtain

$$ S(x) = k_b [(S + 1) \ln (S + 1) - S \ln (S)] N(x) $$

---

We calculate the molar entropy as a function of position using eq 37 for the steady-state distribution obtained with the simulation. We also calculate the entropy with eq 39 using $N(x)$ and $h(x)$ obtained from integrating eqs 12 and 13. Finally, we wish to compare these results with the calculation of the entropy of the steady state resulting from diffusion alone. Using Fick's law, we calculate the distribution $f(n,x)$:

$$N(x) = N(0) = N(L)$$

$$f(n,x) = f(n,0) + (f(n,L) - f(n,0))x/L$$  \hspace{1cm} (40)

Using the definition of $h$ and summing eq 40 term by term, we obtain

$$h(x) = h(0) + (h(L) - h(0))x/L$$  \hspace{1cm} (41)

However, the distribution of polymers at each point is not an equilibrium Flory distribution. Therefore, we must evaluate eq 37 numerically to calculate the entropy. However, we cannot compare directly to the Monte Carlo simulations because of truncation error. (If polymers of more length 100 are used, the CPU time required for the simulations becomes prohibitive.)

We compare the entropies calculated from the integration of eqs 12 and 13 in Figure 4. The steady state resulting from the coupling of diffusion and interchange has a lower entropy and, hence, is more organized than the steady state resulting from diffusion alone. Such self-organization is in accord with the second law of thermodynamics because the system is open. The decrease in entropy between the reservoirs must be more than compensated for by an increase in entropy in the reservoirs.

No autocatalysis occurs in this system and so the self-organization is different from that which occurs in dissipative systems far from equilibrium. The spatial structure occurs because boundary conditions are imposed which result in a molecular flux. Interchange reactions increase the flux. Structures arising from linear flows occur in the near-to-equilibrium regime, in systems such as a linear temperature gradient between two differentially heated boundaries.

Conclusion

We have analyzed the effect of interchange reactions upon the diffusion of a distribution of condensation polymers. Using the analogy of interchange reactions with collisions in a hard-sphere gas, we have formulated the equations analogous to the so-called "hydrodynamic equations" of gas dynamics. We have included the length dependence of the polymer diffusion coefficients and obtained asymptotic solutions and compared them to Monte Carlo simulations of a realistic system.

The steady-state concentration distribution of an interchanging system deviates from a linear distribution resulting from diffusion alone. The length (mass) distribution deviates by 25% from a linear profile. We propose that this deviation could be observed experimentally with UV spectrophotometry and could be used as a test of the Kirkwood–Riseman theory of the length dependence of the diffusion coefficient.

We calculated the entropy of the steady-state distribution and found that it is lower than the distribution in a nonreacting system. The entropy deficit is compensated by an increase in entropy in the reservoirs.

In an open system, interchange reactions have little effect on the molecular and net mass transport of a diffusing polymer distribution.

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Appendix

Two methods were used for simulating the reaction–diffusion equation. One method used a phase space representation and has been described elsewhere. We describe here a one-particle distribution method. In our previous work we used a Monte Carlo method to simulate interchange reactions in a homogeneous system. We have incorporated that algorithm for simulating an extended system.

The algorithm operates as follows: The system is divided into equal volume cells. A cell is selected with the probability proportional to the number of molecules in the cell. Interchange reactions are simulated in that cell as in the homogeneous system. The number of times cells are selected and interchange reactions performed is governed by the parameter $f_m$, which may be a number less than 1. Mass transport is accomplished by selecting a molecule in a cell on the basis of mole fraction contained in each cell, and the molecule is moved to either of the neighboring cells by comparison with a random number. A monomer has a 50% chance of being transported to either neighboring cell. The probability of other species is scaled according to the length dependence function of the diffusion coefficient.

In each iteration, a maximum of one molecule is transported. During a time $\Delta t$, a molecule should move a distance equal to

$$(2D(n)\Delta t)^{1/2}$$  \hspace{1cm} (A.1)

The average distance moved in the simulation is

$$L(N_cN)^{-1}$$  \hspace{1cm} (A.2)

where $N_c$ is the number of cells, $N$ is the total number of molecules, and $N^i$ is the selection probability. By setting (A.1) equal to (A.2), we can solve for $\Delta t$.

$$\Delta t = L/(N_c^22D(n)N)$$  \hspace{1cm} (A.3)

The value of $\Delta t$ is determined by the reaction rate. The average time between reactions is

$$\tau = (2k_{\text{inter}}[P])^{-1}$$  \hspace{1cm} (A.4)

where $[P]$ is the molar concentration of polymer molecules. In the simulation, $\tau$ is related to $\Delta t$ as follows:

$$\tau = N\Delta t(2l\lambda)$$  \hspace{1cm} (A.5)

Setting (A.4) equal to (A.5), we obtain

$$\Delta t = l_c/(k_{\text{inter}}[P]N)$$  \hspace{1cm} (A.6)

The physical time corresponding to one iteration of the simulation is determined by the physical monomer diffusion coefficient. Using eq A.6, $l_c$ is solved for in terms of $k_{\text{inter}}$, $[P]$, and $N$. In the simulations performed $N = 2000$ and $N_c = 20$. The value of $l_c$ equaled 0.005 (corresponding to $k_{\text{inter}} = 10^5$ (M s)$^{-1}$, meaning that the interchange process was performed every 200 diffusion events.

Figure 4. Comparison of the entropy for diffusion alone and with a local Flory equilibrium maintained by interchange reactions. Results were obtained by numerical integration of eqs 12 and 13 with the same boundary conditions as in Figure 3.