

## DISSOCIATION IN A POLYMERIZATION MODEL OF HOMOCHIRALITY

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**Abstract.** A fully self-contained model of homochirality is presented that contains the effects of both polymerization and dissociation. The dissociation fragments are assumed to replenish the substrate from which new monomers can grow and undergo new polymerization. The mean length of isotactic polymers is found to grow slowly with the normalized total number of corresponding building blocks. Alternatively, if one assumes that the dissociation fragments themselves can polymerize further, then this corresponds to a strong source of short polymers, and an unrealistically short average length of only 3. By contrast, without dissociation, isotactic polymers becomes infinitely long.

**Keywords:** DNA polymerization, enantiomeric cross-inhibition, origin of homochirality  
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### 1. Introduction

Central to the question of the origin of life is the polymerization of the first complex molecules that can have catalytic properties and that would eventually carry genetic information. It is widely accepted that our current life form involving DNA carrying the genetic code and RNA producing the proteins that, in turn, catalyze the production of nucleotides, must have been preceded by a simpler life form called the RNA world (Gilbert, 1986; Joyce, 1991; see also Woese, 1967; Crick, 1968; Orgel, 1968; Wattis and Coveney 1999). Here, the RNA has multiple functionality, it carries genetic code and it is also able to catalyze the production of new nucleotides.

The RNA of all terrestrial life forms involves a backbone of dextrorotatory (right-handed) ribose sugars. Theoretically, life could have been equally well based on levorotatory (left-handed) sugars. Unless this selection was somehow externally imposed, e.g. via circularly polarized light (Bailey, 2001), magnetic fields (Thiemann, 1984), or via effects involving the parity-breaking electroweak force (e.g., Hegstrom, 1984), this must have been the result of some bifurcation process. Indeed, the homochirality of left-handed amino acids and of right-handed sugars in living cells can be explained as the result of two combined effects, auto-catalytic production of similar nucleotides during their first polymerization events and a competition between left- and right-handed nucleotides. The general idea goes back to early work of Frank (1953), and has been developed further by Kondepudi and

Nelson (1984), Goldanskii and Kuzmin (1989), Avetisov and Goldanskii (1993) and more recently by Saito and Hyuga (2004a). Of particular interest here is the recently proposed detailed polymerization model of Sandars (2003); see also Brandenburg *et al.* (2005, hereafter referred to as BAHN) and Wattis and Coveney (2005). The main point of Sandars' model is the assumption that the polymerization of monomers of opposite handedness terminates further growth on the corresponding end of the polymer. This is referred to as enantiomeric cross-inhibition. Such inhibition makes it generally quite hard for any polymer to grow successfully. However, once a polymer has become successful in reaching an appreciable length, it will have catalytic properties promoting the production of monomers of the same chirality as that of the catalyzing polymer.

All the polymerization models presented so far ignore the possibility of polymers breaking at an arbitrary location. Without this process polymers would, in the homochiral case, grow to infinite length which is clearly unrealistic. We begin by discussing a model for the dissociation of isotactic polymers, where all the building blocks have the same chirality. Next, we consider the dissociation of polymers whose one end has already been spoiled with a monomer of the opposite chirality. We then incorporate the dissociation model into the full polymerization model of Sandars (2003) and discuss an important modification that is necessary to prevent the average polymer length from being too short.

## 2. Outline of the Model

The model that we are proposing has arisen through the realization that the obvious generalization of the polymerization model of Sandars (2003), to include dissociation, leads to two important difficulties. It was our desire to resolve these problems in a way that seemed most natural to us, and that involves the least amount of assumptions and new parameters. What we came up with is a closed model that is fully self-contained. As in the original model of Sandars, new monomers of either chirality are being produced from an achiral substrate. However, unlike the original model, no external source of the substrate is required. Instead, the substrate can be replenished by the "waste" generated by fragmented polymers.

Before we can discuss the dissociation model, let us explain in a few words the polymerization model of Sandars. Here, polymers can grow by the addition of monomers that can have either the same or the opposite chirality, and the corresponding reaction coefficients are  $k_S$  and  $k_I$ , respectively. The subscript  $S$  indicates that the chirality of both reaction partners is the *same*. The addition of a monomer of opposite chirality leads to the *inhibition* of further growth at that end of the polymer, which is indicated by the subscript  $I$ . The process of such an inhibition, also referred to as "enantiomeric cross-inhibition", is the single most important aspect of the model without which there would be no bifurcation from a racemic (i.e. equally many right- and left-handed building blocks) to a homochiral state.

The fragmentation involves a new parameter: the decay rate  $\gamma_S$ , at which a polymer can break up anywhere in the chain. Again, the subscript  $S$  refers to the situation where the partners involved in the bond have the same chirality. If the chirality is different, we call the decay rate  $\gamma_I$ , in analogy to the corresponding reaction coefficient  $k_I$  in the original polymerization model of Sandars (2003).

The perhaps most obvious assumption for dissociation would be to let the fragments continue to polymerize with new monomers. This leads to two undesired features of the model. In the previous case with only polymerization the homochiral equilibrium had the property that polymers of different lengths are all equally abundant. This goes on all the way to infinity. If we now allow these polymers to break, there is potentially a catastrophe in that arbitrarily many short polymers can form. This is also supported by the numerical simulations discussed below. Furthermore, the numerical solutions show that, even in the best possible case, the average polymer length never exceeds 3, which is clearly unrealistically short. We propose two alternative ways to allow for the formation of longer chains. One possibility is to include an additional degradation of polymers leading to a loss term in the polymerization equations and a corresponding source term for the substrate. Another possibility is to recycle the dissociation products into the substrate without invoking an additional degradation of polymers. In both cases the total number of building blocks in the system is constant, so the substrate plays now an integral part of the model. As a mechanical analogue, we can think of the mass of the substrate as being similar to potential energy, and the mass of all polymers as being similar to kinetic energy, such that the total number (corresponding to the total energy) is conserved. Thus, not only goes the production of new left- and right-handed building blocks at the expense of the substrate, but now the substrate is being replenished by the dissociation fragments such that the total number of building blocks (regardless of their chirality) remains constant.

In the following we develop the model step by step. We first need to show that the mean polymer length is never more than 3 if the fragments are reused for further polymerization.

### 3. Developing the Dissociation Procedure

Following the basic idea behind Sandars' polymerization model we assume the presence of left- and right-handed polymers of length  $n$ , denoted by  $L_n$  and  $R_n$ , respectively. We also assume the presence of polymers whose one end has been spoiled by a reaction with a monomer of opposite chirality. The resulting polymers of this form are denoted by  $L_n R_1$  and  $R_n L_1$ .

#### 3.1. ISOTACTIC DISSOCIATION

We begin with the description of a dissociation model by discussing isotactic polymers of length  $n$ , which are assumed to break (dissociate) at a mean rate  $\gamma_S$  (assumed

independent of  $n$ ), at position  $m$ , according to



Here,  $L$  refers to left-handed building blocks, but a corresponding equation is also valid for right-handed polymers, denoted by  $R$ . In the present case, the fragments  $L_m$  and  $L_{n-m}$  will be reused for further polymerization. As an example,  $L_4$  can break up into two  $L_2$ , or into one  $L_1$  and one  $L_3$ , but for the latter there are two possibilities to do this. Thus, for  $n = 4$  there are altogether  $n - 1 = 3$  different ways of destroying  $L_4$ . This then leads to an evolution equation for the concentration of polymers,  $[L_n]$ ,

$$\frac{d}{dt}[L_n] = \dots + 2\gamma_S \sum_{m=n+1}^N [L_m] - (n-1)\gamma_S[L_n], \quad (2)$$

where  $n \geq 2$ , and the last term represents the decrease of the concentration  $[L_n]$  due to the  $n - 1$  different ways of breaking up the polymer. The first term represents the corresponding gain from breaking up polymers with  $m = n - 1$  or more building blocks. The evolution equation for  $[L_1]$  has only a gain term from breaking up polymers of length  $n \geq 2$ , so

$$\frac{d}{dt}[L_1] = \dots + 2\gamma_S \sum_{n=2}^N [L_n]. \quad (3)$$

The absence of any negative terms (sinks) on the right-hand side implies that, if there is only dissociation,  $[L_1]$  can only grow. The dots in Eqs. (2) and (3) denote the possible presence of extra terms (discussed in the next subsection) that would be needed to model the primary polymerization process.

The same set of Eqs. (2) and (3) applies also to  $R_n$ . The mean rate of dissociation is again  $\gamma_S$ , so the model is completely symmetric with respect to exchanging  $L \rightleftharpoons R$ . Using the identity

$$\sum_{n=1}^N n \sum_{m=n+1}^N [L_n] = \sum_{n=1}^N \frac{1}{2}(n-1)n[L_n], \quad (4)$$

one can easily see that these reaction equations (2) and (3), in the absence of extra terms, conserve the total number of left- and right-handed building blocks, i.e.

$$E_L = \sum_{n=1}^N n[L_n] = \text{const}, \quad E_R = \sum_{n=1}^N n[R_n] = \text{const}. \quad (5)$$

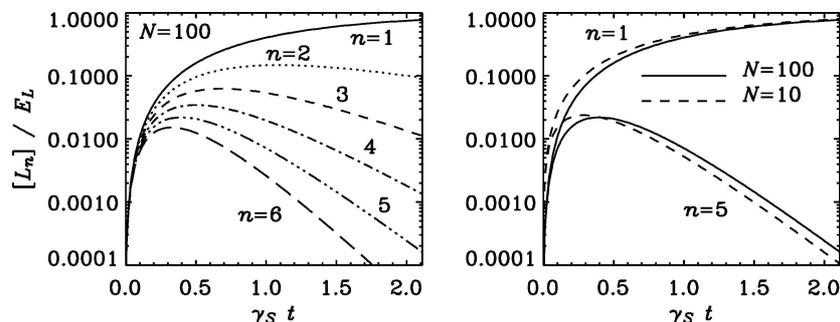


Figure 1. Evolution of  $[L_n]$ , using as initial condition  $[L_{100}] = 1$  and  $[L_n] = 0$  for  $n \neq 100$ .

As an illustration we show in Figure 1 a numerical integration of the evolution of  $[L_n]$ , using as initial condition  $[L_{100}] = 1$  and  $[L_n] = 0$  for  $n \neq 100$ . Thus, we have  $E_L = 100$  initially, and this value is preserved by the model for all times.

As can be seen from Figure 1, both monomers and short polymers are immediately being produced. For  $n \geq 2$  the concentration reaches a maximum at a time that is of the order  $\gamma_S^{-1}$ , and decays then exponentially to zero.

### 3.2. SEMI-SPOILED POLYMERS

For polymers whose one end has been spoiled by a monomer of opposite chirality, we have two types of reactions: those where the spoiling enantiomer breaks off (rate  $\gamma_I$ ) and those where the polymer breaks up somewhere else in the isotactic part (rate  $\gamma_S$ ). Thus, we assume



and



for  $1 \leq m \leq n - 1$ . Ignoring a particular complication that will be discussed in a moment, our *preliminary* set of equations for these additional reactions is then given by

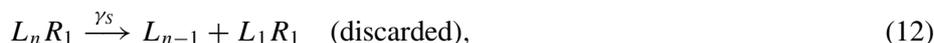
$$\frac{d}{dt}[L_n R_1] = \cdots + \gamma_S \sum_{m=n+1}^N [L_m R_1] - \{\gamma_I + (n-1)\gamma_S\}[L_n R_1], \quad (8)$$

$$\frac{d}{dt}[L_n] = \cdots + \gamma_S \sum_{m=n+1}^N [L_m R_1] + \gamma_I [L_n R_1], \quad (9)$$

$$\frac{d}{dt}[L_1] = \cdots + \gamma_S \sum_{n=2}^N [L_n R_1] + \gamma_I [L_1 R_1], \quad (10)$$

$$\frac{d}{dt}[R_1] = \cdots + \gamma_I \sum_{n=1}^N [L_n R_1]. \quad (11)$$

These equations ignore the dissociation of isotactic polymers discussed in the previous section, but they can simply be added to the present set of equations. Again, the system of equations has to be completely symmetric with respect to exchanging  $L \rightleftharpoons R$ . However, the reaction (7) for  $m = n - 1$  produces  $L_1 R_1$  at a rate that is proportional to  $[L_n R_1]$ . In general, since  $[L_n R_1] \neq [R_n L_1]$ , this would lead to  $[L_1 R_1] \neq [R_1 L_1]$ , which is not permitted. We therefore have to discard the reaction (7) for  $m = n - 1$ , i.e. we have to discard the reactions



and likewise for the dissociation of  $R_n L_1$ . Since we have therefore one reaction less, this means that in Eq. (8), which now applies only for  $n \geq 2$ , the  $n - 1$  factor changes effectively into a  $n - 2$  factor. Furthermore, in Eqs. (9) and (10) the sums start only with  $m = n + 2$  and  $n = 3$ , respectively.

When writing down the full set of equations we have to treat the evolution of  $[L_1 R_1]$  separately, so

$$\frac{d}{dt}[L_1 R_1] = \cdots - \gamma_I [L_n R_1], \quad (13)$$

while for  $n \geq 2$  we have a pair of equations

$$\frac{d}{dt}[L_n R_1] = \cdots + w_n^{(LR)} - \{\gamma_I + (n - 2)\gamma_S\}[L_n R_1], \quad (14)$$

$$\frac{d}{dt}[R_n L_1] = \cdots + w_n^{(RL)} - \{\gamma_I + (n - 2)\gamma_S\}[R_n L_1]. \quad (15)$$

Here,

$$w_n^{(LR)} = \gamma_S \sum_{m=n+1}^N [L_m R_1], \quad w_n^{(RL)} = \gamma_S \sum_{m=n+1}^N [R_m L_1], \quad (16)$$

are all the terms that have resulted from dissociation. The corresponding pair of equations for  $[L_n]$  and  $[R_n]$  is automatically valid also for  $n = 1$ , so we have

$$\frac{d}{dt}[L_n] = \cdots + w_n^{(L)} - (n - 1)\gamma_S [L_n], \quad (17)$$

$$\frac{d}{dt}[R_n] = \cdots + w_n^{(R)} - (n - 1)\gamma_S [R_n], \quad (18)$$

where

$$w_n^{(L)} = 2\gamma_S \sum_{m=n+1}^N [L_m] + \gamma_S \sum_{m=n+2}^N [L_m R_1] + \gamma_I [L_n R_1] + \delta_{n1} \sum_{m=1}^N [R_m L_1], \quad (19)$$

$$w_n^{(R)} = 2\gamma_S \sum_{m=n+1}^N [R_m] + \gamma_S \sum_{m=n+2}^N [R_m L_1] + \gamma_I [R_n L_1] + \delta_{n1} \sum_{m=1}^N [L_m R_1]. \quad (20)$$

Here,  $\delta_{n1} = 1$  for  $n = 1$ , and  $\delta_{n1} = 0$  for  $n \geq 2$ .

We have calculated solutions using as initial condition  $[L_n R] = 1$  for different values of  $n$  and found that the evolution of  $[L_n]$  is very similar to that shown in Figure 1, so we do not need to reproduce this result here.

### 3.3. POLYMERIZATION AND DISSOCIATION

We now add the polymerization equations of Sandars (2003) to Eqs. (13)–(18). Again, we begin by discussing first the homochiral case. In that case we have only two reactions,



where  $k_S$  is the reaction coefficient for attaching a monomer with the same handedness. The factor 2 on  $k_S$  indicates that polymerization can proceed on both ends of the polymer. This agrees with earlier approaches, and may be realistic for PNA polymerization, but not for RNA or DNA polymerization which usually proceeds only on one end. Since the monomer can be attached to any one of the two ends of the polymer, the overall reaction proceeds with the coefficient  $2k_S$ . The full reaction equations for the homochiral case can then be written as (for  $n \geq 3$ )

$$\frac{d[L_n]}{dt} = 2k_S [L_1] ([L_{n-1}] - [L_n]) + 2\gamma_S \sum_{m=n+1}^N [L_m] - (n-1)\gamma_S [L_n], \quad (23)$$

while for  $n = 2$  we have

$$\frac{d[L_2]}{dt} = k_S [L_1] ([L_1] - 2[L_2]) + 2\gamma_S \sum_{m=3}^N [L_m] - \gamma_S [L_2], \quad (24)$$

where an extra  $1/2$  factor has occurred in front of the  $[L_1]^2$  term. (For  $n = 2$ , two pieces of the same species react with each other, whereas for  $n > 2$  there are always

two different species, i.e. monomers and polymers; see BAHN for a more detailed discussion). For  $n = 1$  we have

$$\frac{d}{dt}[L_1] = -2k_S[L_1] \sum_{n=1}^{N-1}[L_n] + 2\gamma_S \sum_{n=2}^N[L_n]. \quad (25)$$

Note that this problem is governed by three parameters,  $k_S$ ,  $\gamma_S$ , and the conserved quantity  $E_L$ , which only depends on the initial condition. These three parameters can be combined into a single non-dimensional parameter,

$$\mathcal{M} = E_L k_S / \gamma_S \quad (\text{homochiral case}), \quad (26)$$

that characterizes all possible solutions. Moreover, these equations possess a unique equilibrium state which is in general different for different values of  $\mathcal{M}$ ; see Figure 2. Here we have normalized  $[L_n]$  in terms of  $\gamma_S/k_S$  to make it dimensionless.

Given that there is a non-dimensional parameter ( $\mathcal{M}$ ) in the problem, there is no unique choice for a non-dimensional representation of time. Possible non-dimensional combinations are  $\gamma_S t$  (as used in Figure 1) and  $E_L k_S t$ . In Figure 3 we show the time dependence of  $[L_4]$  (normalized by  $E_L$ ) as a function of  $\gamma_S t$  toward the equilibrium solution shown in Figure 2. Note that the approximate position of the maximum is always at around the same value of  $\gamma_S t$  for values of  $\mathcal{M}$  changing over six orders of magnitude. This shows that the typical relaxation time scale is governed by  $\gamma_S^{-1}$ .

It is somewhat surprising that with dissociation,  $[L_n]$  always peaks at small values of  $n$  (at  $n = 2$  for  $\mathcal{M} \geq 10$  or at  $n = 1$  for smaller values of  $\mathcal{M}$ ). This can be quantified in terms of the mean polymer length  $N_L$  that can be defined as  $N_L = \sum n[L_n] / \sum [L_n]$  (see BAHN). The resulting values of  $N_L$  approach 3 for large values of  $\mathcal{M}$ , but are otherwise always less than 3.

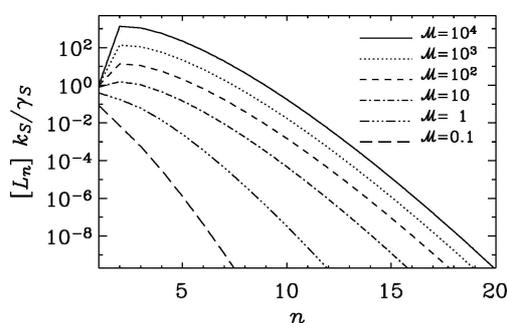


Figure 2. Isotactic equilibrium states with polymerization and dissociation, for different values of the universal parameter  $\mathcal{M}$  changing over a range of six orders of magnitude.

TABLE I

Mean polymer length  $N_L$  for different values of  $\mathcal{M}$ , for isotactic polymers (here left-handed)

$\mathcal{M}$	0.1	1	10	$10^2$	$10^3$	$10^4$
$N_L$	1.09	1.55	2.45	2.92	2.99	3.00

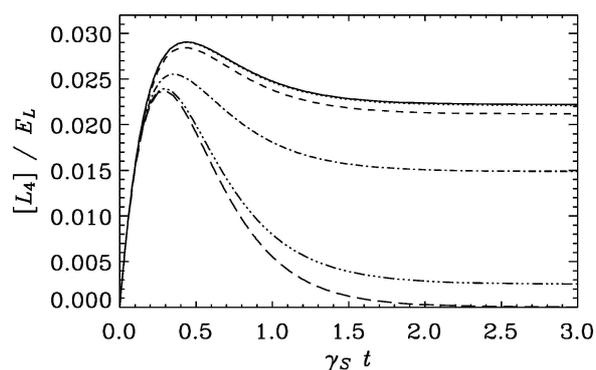


Figure 3. Relaxation phase toward the isotactic equilibrium states in the presence of polymerization and dissociation, for the same six different values of the parameter  $\mathcal{M}$  as in Figure 2.

### 3.4. COUPLING TO A SUBSTRATE

It is natural to proceed as in the model of Sandars (2003) and couple the polymerization equation to a substrate from which new monomers can be produced in a catalytic fashion. It is sufficient to discuss first the isotactic case, so we add a source  $Q_L$  to the right-hand side of Eq. (25),

$$\frac{d}{dt}[L_1] = Q_L - 2k_S[L_1] \sum_{n=1}^{N-1} [L_n] + 2\gamma_S \sum_{n=2}^N [L_n], \quad (27)$$

where  $Q_L$  quantifies the source of new left-handed monomers. Since this term provides of source of left-handed building blocks,  $E_L$  is no longer conserved. Instead, as discussed by BAHN,  $E_L$  obeys the evolution equation

$$\frac{dE_L}{dt} = Q_L - 2k_S[L_1][L_N]. \quad (28)$$

In the absence of dissociation, a homochiral steady state is possible, where  $[L_n]$  is constant for all  $n \geq 2$ , so  $[L_N]$  is finite and  $Q_L$  is balanced by  $2k_S[L_1][L_N]$ .

Obviously,  $Q_L$  should depend on the concentration of the substrate,  $[S]$ , so it is natural to write  $Q_L = k_C[S]C_L$ , where  $C_L$  determines the efficiency of the production of left-handed monomers from the substrate. (For imperfect fidelity,

$f < 1$ , of the catalyst the source  $Q_L$  can also have a fractional contribution from  $C_R$ ; see Eqs. (11) and (12) of BAHN.) Since this generation is supposed to be a catalytic process,  $C_L$  should depend in some way on  $[L_n]$  itself; here we assume  $C_L = E_L$ , but different proposals have been made in the past (see BAHN for a discussion). The substrate itself obeys an evolution equation of the form

$$\frac{d[S]}{dt} = Q - (Q_L + Q_R), \quad (29)$$

where  $Q$  is a source for the substrate. For the moment, this source can be thought of as being externally given, as in the model of Sandars (2003), but we will assume that this comes actually from the dissociation fragments.

Regardless of the particular choice, we face a general problem in that dissociation causes the polymers to have finite length, so  $[L_N] \rightarrow 0$  and hence no equilibrium state is possible any more. This causes a secular (linear) growth, so at some point the numerical integration develops an arithmetic overflow. An obvious way to balance this secular growth is to add a simple loss term,  $d[L_n]/dt = \dots - \gamma[L_n]$ , where  $\gamma$  is the degradation rate and the dots denote all the other terms that are already present. The result is shown in Figure 4.

### 3.5. FEEDING THE FRAGMENTS BACK INTO THE SUBSTRATE

Clearly, the dissociation model developed so far requires some modifications that are necessary to prevent the model from displaying secular growth when combined with the polymerization model of Sandars (2003) and to allow for an average polymers length of more than 3. One possibility would be to make the decay rate  $\gamma_S$  dependent on  $n$ , for example in such a way that  $\gamma_S = 0$  for small values of  $n$ . One could also think of adding an overall loss term. Yet another possibility, that is close to our final proposal, is to recycle the monomers resulting from dissociation back into the substrate. In the end, however, we found it most plausible to assume that all fragments resulting from dissociation are recycled back into the achiral substrate.

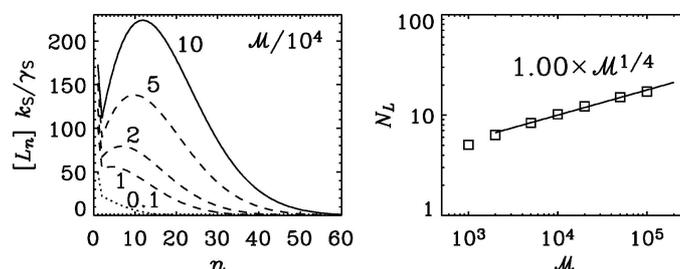


Figure 4. Isotactic equilibrium states with polymerization, dissociation, and uniform degradation, for different values of  $M/10^4$  (left), and the mean polymer length  $N_L$  (right), for  $\gamma/\gamma_S = 20$ .

Thus, the source term would then be

$$Q = W_L + W_R + W_{LR} + W_{RL} + W_{RLR} + W_{LRL}, \quad (30)$$

where

$$W_L = \sum_{n=1}^N n w_n^{(L)}, \quad W_R = \sum_{n=1}^N n w_n^{(R)}, \quad (31)$$

is the total number of recycled building blocks (both left-handed and right-handed),

$$W_{LR} = \sum_{n=1}^N (n+1) w_n^{(LR)}, \quad W_{RL} = \sum_{n=1}^N (n+1) w_n^{(RL)} \quad (32)$$

are the corresponding contributions from fragmented semi-spoiled polymers, and

$$W_{RLR} = \sum_{n=2}^N (n+2) [R_1][L_n R], \quad W_{LRL} = \sum_{n=2}^N (n+2) [L_1][R_n L] \quad (33)$$

are the contributions from terminally spoiled chains. The new system of equations is then

$$\frac{d}{dt}[L_n] = p_n^{(L)} - (n-1)\gamma_S[L_n], \quad (34)$$

$$\frac{d}{dt}[R_n] = p_n^{(R)} - (n-1)\gamma_S[R_n], \quad (35)$$

$$\frac{d}{dt}[L_n R_1] = p_n^{(LR)} - \{\gamma_I + (n-2)\gamma_S\}[L_n R_1], \quad (36)$$

$$\frac{d}{dt}[R_n L_1] = p_n^{(RL)} - \{\gamma_I + (n-2)\gamma_S\}[R_n L_1], \quad (37)$$

where  $p_n^{(L)}$ ,  $p_n^{(R)}$ ,  $p_n^{(LR)}$ , and  $p_n^{(RL)}$  indicate the terms due to polymerization (see Sandars, 2003, BAHN, Wattis and Coveney, 2005); see the appendix. Equations (34) and (35) are valid for all  $n \geq 1$ , but Eqs. (36) and (37) are only valid for  $n \geq 2$ . For  $n = 1$  these equations reduce to

$$\frac{d}{dt}[L_1 R_1] = p_1^{(LR)} - \gamma_I[L_1 R_1]. \quad (38)$$

We note that  $[R_1 L_1] = [L_1 R_1]$ . These equations are constructed in such a way that the total number (or mass) of right- and left-handed building blocks is conserved, i.e.

$$M \equiv [S] + E_R + E_L + E_R^+ + E_L^+ = \text{const.} \quad (39)$$

Here,  $E_R^\pm = \sum(n \pm 1)[R_n]$  and  $E_L^\pm = \sum(n \pm 1)[L_n]$  have been introduced. We recall that due to recycling of the right- and left-handed building blocks through an achiral substrate, the total chirality, which involves  $E_R^-$  and  $E_L^-$ , is not conserved; see Section 5 of BAHN. The quantity  $\mathcal{M}$  can be expressed in non-dimensional form,

$$\mathcal{M} = Mk_S/\gamma_S \quad (\text{general case}), \quad (40)$$

which is conserved for all times. This is therefore the main control parameter of our model. It generalizes our earlier definition for the fully homochiral cases; see Eq. (26).

In Figure 5 we show that increasing the value of  $\mathcal{M}$  leads to an increased range over which the racemic solution is unstable and a near-homochiral state emerges. Likewise, increasing the rate at which the spoiling monomers break off also broadens the range of permissible values of the fidelity for which the racemic solution is unstable.

When  $f$  exceeds a critical value, the enantiomeric excess

$$\eta = \frac{E_L - E_R}{E_L + E_R} \quad (41)$$

increases exponentially with time like  $e^{\lambda t}$ , where  $\lambda$  is the growth rate. For  $f = 1$ , the growth rate is (see Figure 6)  $\lambda = 1.2\mathcal{M}^{1/2}\gamma_S \equiv (Mk_S\gamma_S)^{1/2}$ , so it is the geometrical mean between the polymerization rate  $Mk_S$  on the one hand and the dissociation rate  $\gamma_S$  on the other.

Contrary to the model without recycling, the present model does allow for polymer lengths that can easily exceed the previous bound of 3. This requires large values of  $\mathcal{M}$ ; see Figure 6, where we plot the resulting values of  $N_L$  as a function

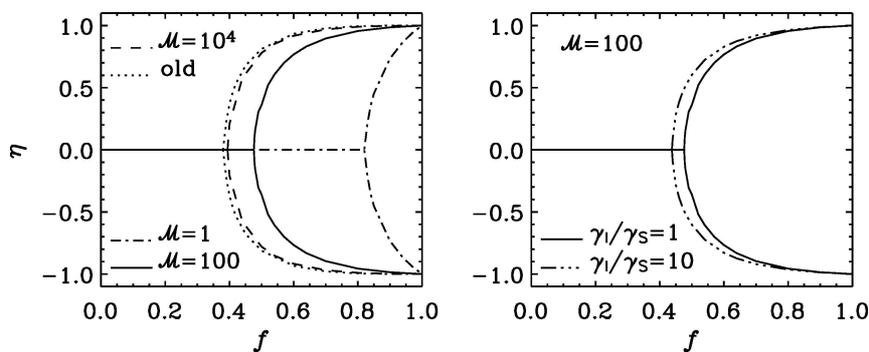


Figure 5. The effects of  $\mathcal{M}$  and  $\gamma_I$  on the bifurcation diagram. Increasing the values of  $\mathcal{M}$  and  $\gamma_I$  allow near-homochiral states with decreased fidelity.

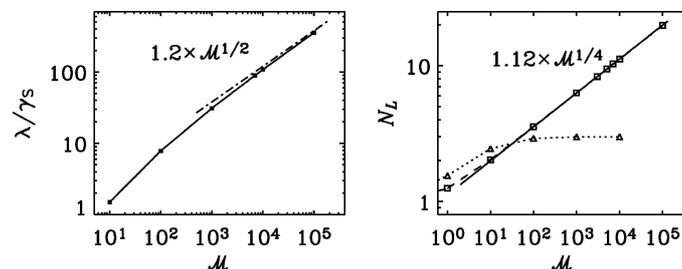


Figure 6. Dependence of normalized growth rate  $\lambda/\gamma_S$  for the racemic solution and mean polymer length  $N_L$  for the homochiral solution on the total normalized mass parameter  $\mathcal{M}$  for  $f = 1$ ,  $k_I/k_S = 1$  and  $\gamma_I/\gamma_S = 1$ . The dotted line corresponds to the data of Table I, where the fragments are not recycled back to the substrate.

of  $\mathcal{M}$ . In fact, we find that to a good approximation,

$$N_L \text{ or } N_R \approx 1.12\mathcal{M}^{1/4} \quad (\text{for } \mathcal{M} \geq 10); \quad (42)$$

see Figure 6. We regard the possibility of long chains as a crucial property of any reasonable polymerization model. Furthermore, the fact that the model is now fully self-contained ( $M$  is conserved) makes it an appealing alternative to previous models.

#### 4. Conclusions

Dissociation of polymers appears to be an important component of any polymerization model. The present work has shown, however, that the straightforward usage of dissociation fragments for further polymerization does not yield realistic model behavior, because the maximum polymer length would not be more than 3. Various other modifications that could allow for longer polymers have been discussed, and it is likely that there are more possibilities. The main problem is that the fragments from dissociation tend to produce excessive amounts of short polymers that cause the average polymer length to be very short. Consequently, we have postulated that the fragments resulting from polymerization are instead recycled into the substrate. The average polymer length then depends on the normalized dissociation time. In this model, no external source of the substrate is required, so the model is now fully self-contained.

The model is governed by the total number of left- and right-handed homochiral building blocks, the reaction rates for polymerization with the same and the opposite chirality, and the corresponding dissociation rates. These numbers can be combined into a single non-dimensional number that characterizes the behavior of the system. At the moment we have no clear idea about its value, but laboratory experiments should be able to determine not only this coefficient, but they should also allow us to test various aspects and predictions of the model.

We recall that in order to draw conclusions about the time scale on which homochirality can be achieved, it is important to discuss the spatial extent of the system (Saito and Hyuga 2004b). Homochirality may develop rapidly at one point in space, but the handedness may be different at different locations. The relevant time scale for achieving global homochirality is therefore much longer and is given either by the diffusion time scale, which is very long, or by a turbulent turnover time which can be much shorter if turbulent flows are present (Brandenburg and Multamäki, 2004). Obviously, the generalizations given in the present paper can directly be applied to their model provided the local growth remains still large enough.

### Appendix A. Polymerization Terms

In this appendix we state the terms describing the polymerization process. These terms enter in Eqs. (34)–(38) in Section 3.5 and are equivalent to those given and discussed in BAHN, Eqs. (20)–(27). For  $n \geq 2$  we have

$$p_n^{(L)} = 2k_S[L_1](\sigma_n^{(1/2)}[L_{n-1}] - [L_n]) - 2k_I[L_n][R_1], \quad (43)$$

$$p_n^{(R)} = 2k_S[R_1](\sigma_n^{(1/2)}[R_{n-1}] - [R_n]) - 2k_I[R_n][L_1], \quad (44)$$

$$p_n^{(RL)} = k_S[R_1](\sigma_n^{(0)}[R_{n-1}L] - [R_nL]) + k_I[L_1](2[R_n] - [R_nL]), \quad (45)$$

$$p_n^{(LR)} = k_S[L_1](\sigma_n^{(0)}[L_{n-1}R] - [L_nR]) + k_I[R_1](2[L_n] - [L_nR]), \quad (46)$$

whereas for  $n = 1$  we have  $p_1^{(L)} = -\lambda_L[L_1]$  and  $p_1^{(R)} = -\lambda_R[R_1]$ , where

$$\lambda_L = 2k_S \sum_{n=1}^{N-1} [L_n] + 2k_I \sum_{n=1}^N [R_n] + k_S \sum_{n=2}^{N-1} [L_nR] + k_I \sum_{n=2}^N [R_nL], \quad (47)$$

$$\lambda_R = 2k_S \sum_{n=1}^{N-1} [R_n] + 2k_I \sum_{n=1}^N [L_n] + k_S \sum_{n=2}^{N-1} [R_nL] + k_I \sum_{n=2}^N [L_nR], \quad (48)$$

and  $p_1^{(RL)} = p_1^{(LR)} = 0$ .

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