Amplification of Chirality in Helical Supramolecular Polymers: The Majority-Rules Principle

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ABSTRACT: Amplification of chirality, being a strongly nonlinear response of the optical activity of helical polymers to a small (net) amount of optically active material, has recently been discovered in supramolecular copolymers. Apart from the sergeants-and-soldiers type we discussed in earlier work, chirality amplification can also occur in copolymers consisting of the two enantiomeric forms of the monomeric building blocks. We outline the first theoretical treatment of this “majority-rules” type of chirality amplification in self-assembled aggregates. Our treatment, which is based on the one-dimensional, two-component Ising model, is analytical and exact in the infinite-chain limit. We find a strong dependence of the strength of the chirality amplification on the free-energy penalty of a helix reversal as well as on that of a mismatch between the preferred helical handedness of a monomer and the actual screw sense of the bond that follows it. The strength of the chirality amplification shows a monotonic increase with increasing helix reversal penalty but a strongly nonlinear and nonmonotonic dependence on the mismatch penalty.

I. Introduction

Amplification of chirality is a well-known phenomenon in solutions of helical copolymers.[1,2] Of the two classes of chirality amplification, the sergeants-and-soldiers type has been studied most extensively, while the majority-rules type is somewhat less well-known. The sergeants-and-soldiers principle is characterized by a strongly nonlinear response of the optical properties of the (achiral) polymers to the addition of a small amount of homochiral material,[3] whereas the majority-rules principle represents a similar effect for chains consisting of both enantiomeric forms of the chiral monomers, one of which is present in (small) excess.[4] Both effects occur due to a shift in the balance between left- and right-handed helical bonds, which can be quite large.

Recently, strong chirality amplification of the sergeants-and-soldiers type was found in solutions of self-assembled helical aggregates by measurements of the optical activity.[5,6] This is remarkable, since the monomeric units in these aggregates are linked by relatively weak bonds, making the aggregates in a way quite fragile. In earlier work, we found that the sergeants-and-soldiers principle in such self-assembled systems can be accurately described in terms of a one-dimensional, two-component Ising model.[7,8] In this paper we modify this model to describe the majority-rules principle in long supramolecular polymers. The reason that a similar model may be used is that the same physical principles are at work in both the majority-rules and the sergeants-and-soldiers case. In both cases, the polymers consist of two types of monomer, which can be bound in two ways (either by a left-handed helical bond or by a right-handed one). In addition, both phenomena find their origin in the cooperativity of the helical aggregation. However, as we shall see below, for a description of the majority-rules type of chirality amplification we need two free-energy penalties rather than one. This makes this treatment somewhat more involved than the one we applied in refs 7 and 8.

Note that our treatment is not the first to describe the majority-rules effect. In a recent paper,[9] Selinger and Selinger investigate the majority-rules principle in conventional (covalently bound) polymers by applying a random-field Ising model. Unfortunately, the existing theory cannot be applied to supramolecular systems, at least not in principle, since the distribution of the two types of monomer along the chains is fixed in conventional polymers, whereas in supramolecular aggregates it is determined by the thermodynamic equilibrium. Our treatment is specifically suited to describe chirality amplification in supramolecular polymers and is analytical and exact in the infinite-chain limit.

The remainder of this paper is organized as follows. In section II we outline our model for the majority-rules effect in dilute solutions of long supramolecular polymers, and in section III we calculate the net helicity (defined as the difference between the fractions of right- and left-handed bonds of a polymer) as a function of the enantiomeric excess (defined as the difference between the fractions of right- and left-handed chiral monomers). In section IV we present our results and demonstrate that the amplification of chirality increases strongly with an increasing free energy penalty on a helix reversal. We also show the nonmonotonic dependence of the chirality amplification on the free energy of a mismatch between the preferred screw sense of a monomer and the bond that follows it. Finally, in section V we summarize our findings and give a brief outlook.

II. The Single-Aggregate Partition Function

In our description we consider a dilute solution of aggregates, so that we may ignore interaggregate interactions. We assume that the aggregates are long, and discard finite-size effects, allowing us to describe the configurational statistics of polymers with a rela-

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tively straightforward ground-state calculation. It seems reasonable to suggest that long-range intraaggregate interactions are unimportant for the problem in hand. Presuming that the amplification of chirality is dominated by interactions on small length scales, such as nearest-neighbor interactions, we can rely on a two-state Ising model in one dimension to properly describe the conformational state of the aggregates.[7,10]

We make a distinction between two types of monomer: a chiral monomer that has a preferred left-handed screw sense (which we shall abbreviate as a "−" monomer) and one that has a preferred right-handed screw sense (the "+ " monomer). These monomers can be linked in two ways: one corresponding to a right-handed helical conformation and one corresponding to a left-handed one. These ways of bonding we refer to as the "+" bond, which is the bond type most compatible with the "+" monomer, and the "−" bond, which is most compatible with the "−" monomer. Furthermore, we introduce two free-energy penalties, R and W: the first penalizes a helix reversal along the chain, and the second penalizes a mismatch between the preferred screw sense of a monomer and the bonds near to it. The former penalty is invoked when two consecutive bonds have different conformations, and the latter is used whenever a "+" bond follows or precedes a "−" monomer, and vice versa. We apply the mismatch penalty twice when both monomers surrounding a bond are of the type incompatible with that bond. These energies, and all other energies in this paper, are given in units of k_BT, with k_B being Boltzmann's constant and T the absolute temperature.

Our model corresponds to the following dimensionless Hamiltonian H for a chain of degree of polymerization N.

$$H = \frac{1}{2}R\sum_{j=1}^{N-2}(-s_js_{j+1} + 1) + \frac{1}{2}P\sum_{j=1}^{N-1}(s_j + 1) + W\sum_{j=1}^{N-1}\left[1 - \frac{1}{2}(s_jn_j + s_jn_{j+1})\right] - E(N - 1) \quad (1)$$

Here, s_j gives the state of the jth spin (or bond), with $s_j = -1$ for a "down" spin (a "−" bond) and $s_j = +1$ for an "up" spin (a "+" bond), and n_j gives the type of the jth monomer, with $n_j = -1$ for a "−" monomer and $n_j = +1$ for a "+" monomer. The quantity P corresponds to the magnetic-field strength in the Ising model and couples to the "up" spins, and $-E$ is the reference bond free energy. Note that the Hamiltonian (eq 1) is only valid for chains of length $N \geq 3$, which is indeed the regime we wish to describe.

The (quasi-grand canonical) partition function of a single aggregate now reads

$$\Xi(N) \equiv \left(\prod_{k=1}^{N}\sum_{n_{k=\pm1}}\right)\exp\left[\mu_-\left(N - \frac{1}{2}\sum_{j=1}^{N}(n_j + 1)\right) + \frac{1}{2}\mu_+\sum_{j=1}^{N}(n_j + 1)\right]\left(\prod_{l=1}^{N\text{-}1}\sum_{s_{l=\pm1}}\right)\exp(-H) \quad (2)$$

Here, the first and last bracketed terms are repeated sums, μ_- is the chemical potential of the "−" monomers, and μ_+ is that of the "+" monomers. We use a quasi-grand partition function here, in which the total number of monomers in the chain is kept fixed at N, while the chain composition can change. This partition function is evaluated with the aid of the well-known transfer matrix method. The transfer matrix contains the statistical weights for all configurations of a monomer-bond pair, dependent on the monomer-bond pair preceding it. The matrix can be derived from the Hamiltonian (eq 1) by standard methods.[11] For this, it turns out to be convenient to redefine the chemical potentials, so that we obtain a reference chemical potential (equal to μ_-) and an excess chemical potential, defined as $\mu \equiv \mu_+ - \mu_-$. We now define a fugacity $z \equiv \exp(\mu)$ that we introduce into the transfer matrix whenever a "+" monomer is considered. (See ref 8 for a formal derivation of a transfer matrix including these chemical potentials.) The aggregate can be divided into two sublattices: one that contains the monomers (with states +1 and −1) and one that contains the bonds (also with states +1 and −1). Taking into account the interactions between the two sublattices, the transfer matrix becomes the sum of four matrices, one for each possible combination of monomers preceding and following the bond under consideration. It takes the final form

$$\mathbf{M} = \begin{pmatrix} (1 + w)(zw + 1) & (1 + w)(zw + 1)\sqrt{\sigma} \\ s\sqrt{\sigma}(1 + w)(w + z) & s(1 + w)(w + z) \end{pmatrix} \quad (3)$$

with $s \equiv \exp(-P)$ and $w \equiv \exp(-W)$ the Boltzmann factors of an "up" spin (over a "down" one) and that of a mismatch between a bond and a monomer, and $\sigma \equiv \exp(-2R)$ the squared Boltzmann factor of a helix reversal. In the matrix representation we can rewrite the partition function $\Xi(N)$, eq 2,[8] giving

$$\Xi(N) = \exp[\mu_-N + E(N - 1)]\tilde{\mathbf{u}}\cdot\mathbf{M}^{N-2}\cdot\tilde{\mathbf{u}}^+ \quad (4)$$

The quantities $\tilde{\mathbf{u}}$ and $\tilde{\mathbf{u}}^+$ are the vectors that describe the probability distribution over the states of the aggregate ends. Since our treatment is meant to describe the long-chain limit, we need not specify these.

III. Ground-State Approximation

To make the partition function explicit, we determine the eigenvalues of $\mathbf{M}$. These are $\lambda_{1,2} = \frac{1}{2}(1 + w)(1 + zs + zw + sw \pm \sqrt{\alpha})$, where λ_1 is given by the plus sign and λ_2 by the minus sign. Here, $\alpha = (zw + 1 - sw - sz)^2 + 4\sigma(zw + 1)(sw + sz)$. The partition function now becomes a sum of two terms, each including one of the eigenvalues. In the long-chain limit, the term which includes λ_1 is much larger than that which contains λ_2. We can therefore use the so-called ground-state approximation and retain only this term.[12] The partition function then becomes

$$\Xi(N) \approx A(s,\sigma,w,z)\exp[\mu_0N + E(N - 1)]\lambda_1^{\,N} \quad (5)$$

Here, A is a prefactor that contains end effects and as such does not contribute in a significant way in the long-chain limit. Formally, eq 5 is only valid for $N \gg 1$, becoming exact in the infinite-chain limit, but we extrapolate it down to $N > 2$. This is allowed if the mean degree of polymerization, $\langle N\rangle \simeq \sqrt{\phi\exp(\epsilon)}$, remains large; here ϕ is the volume fraction of aggregating molecules and $\epsilon \equiv E - \ln A(s,\sigma,w,z)$ is the free-energy penalty associated with the aggregate ends (the so-called end-cap energy).[12] In the long-chain regime, the mass distribution of the aggregates is fairly sharply peaked around $N = \langle N \rangle$. This means that we need not deal explicitly with the self-assembly, and we can represent the (concentration- and temperature-dependent) mean value $\langle N \rangle$ by N in the remainder of this paper.

From the partition function we can obtain the quantities that determine the strength of the chirality amplification, being the net helicity (the fraction right-handed minus the fraction left-handed helical bonds) and the enantiomeric excess x (the fraction of "+" monomers minus that of "− " monomers). These are given by

$$\eta \equiv -1 + 2(N-1)^{-1}\, \partial \ln \Xi(N)/\partial \ln s \sim -1 + 2\frac{s}{\lambda_1}\, \partial\lambda_1/\partial s \quad (6)$$

$$x \equiv -1 + 2N^{-1}\, \partial \ln \Xi(N)/\partial \ln z \sim -1 + 2\frac{z}{\lambda_1}\, \partial\lambda_1/\partial z \quad (7)$$

These limiting equations become exact for infinitely long chains. Since right-handed bonds are not intrinsically more or less favorable than left-handed ones, we now set $s = 1$ by symmetry and simplify eqs 6 and 7. The net helicity η and enantiomeric excess x become

$$\eta = \frac{(z-1)(1-w)}{\sqrt{\alpha}} \quad (8)$$

$$x = \frac{(z-1)(1+w)\sqrt{\alpha} + 4w\sigma(z^2-1) + (z^2-1)(1-w)^2}{[(z+1)(1+w)+\sqrt{\alpha}]\sqrt{\alpha}} \quad (9)$$

with α as defined earlier in this section. In principle, we can now eliminate z from eqs 8 and 9 and express x in terms of η, σ, and w. However, we found it more convenient to numerically solve z from eq 8 for fixed values of w, η, and σ and insert the obtained value for z back into eq 9 to obtain x. We discuss the results of this procedure in the next section. We limit our discussion to the regime where the fraction of "+" monomers is equal or larger than the fraction of "−" monomers. Since the majority-rules effect is symmetrical, the results for a majority of "−" monomers would be identical, albeit that η, as defined in eq 6, would become negative.

IV. Results and Discussion

Let x_* be defined as the enantiomeric excess needed to induce a net helicity of one-half. It is a measure of the strength of the chirality amplification, in that the lower x_* is, the more monomers are influenced by a single "+" monomer. To investigate the impact of the various free-energy penalties on this quantity, we plot it in Figure 1, against the squared Boltzmann factor of a helix reversal σ, for different values of the Boltzmann factor w of a mismatch. The figure shows that, for fixed low values of σ (and hence high values for the free energy of a helix reversal), the strength of the chirality amplification increases monotonically with increasing value of the Boltzmann factor of a mismatch. This is because in this regime (where helix reversals are very unfavorable) the lower the mismatch free energy is, the more "−" monomers can be present in the aggregates without changing the net helicity. In this low-σ regime, the degree of chirality amplification becomes insensitive to the value of σ (especially for low w), as indicated by the horizontal curves. Apparently, the chirality amplification is dominated by the value of w here, whereas for higher values of σ, the free-energy penalty of a helix reversal becomes more important.

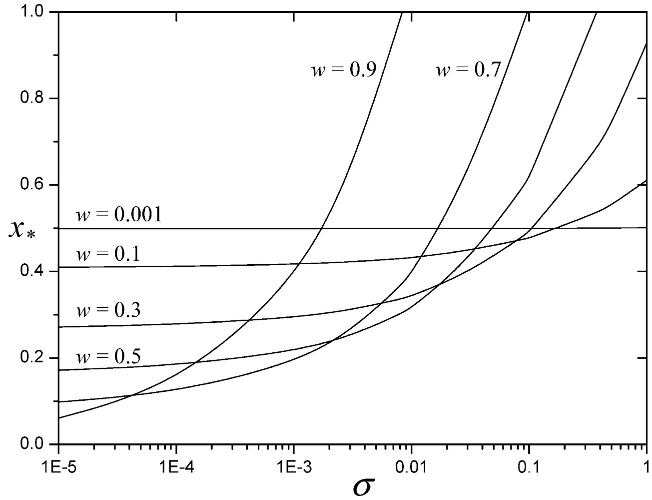

Figure 1. Excess fraction of "+" chiral material needed to attain a net helicity of one-half, x_*, vs $\sigma = \exp(-2R)$, with R the free-energy penalty of a helix reversal, for six values of the mismatch parameter w, as indicated.

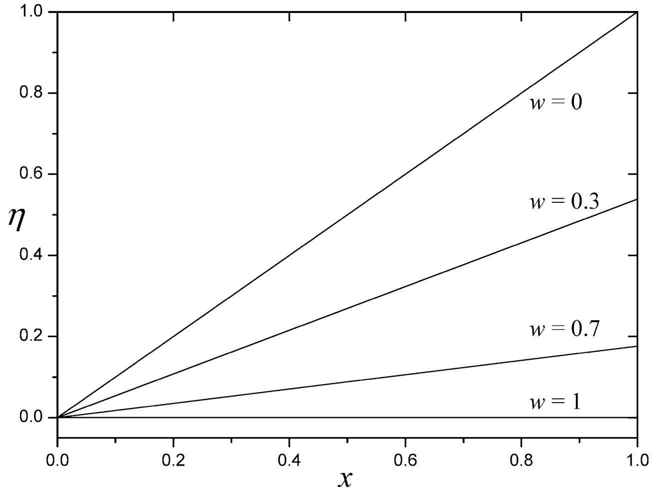

Figure 2. Net helicity η as a function of the enantiomeric excess x, for different values of the mismatch parameter w as indicated, at a fixed value of the free energy of a helix reversal of zero ($\sigma = 1$).

When we look at the high-σ regime, we observe that the amplification of chirality is lower than in the low-σ regime; for $\sigma = 1$ there is no longer any amplification of chirality. For values of w close to unity, it is even so that a net helicity of one-half cannot be reached, even if only "+" monomers are present.

We now look at the chirality amplification for two values of σ in more detail by taking vertical cuts through the diagram. To this end, we first consider the case $\sigma = 1$ (implying no penalty on helix reversals) (see Figure 2). In this case, as may in fact already be concluded from Figure 1, we notice that there is indeed no chirality amplification. It follows from eqs 8 and 9 that

$$\eta = \left(\frac{1-w}{1+w}\right)x \quad (10)$$

This is a linear function of x, and an increase in w from

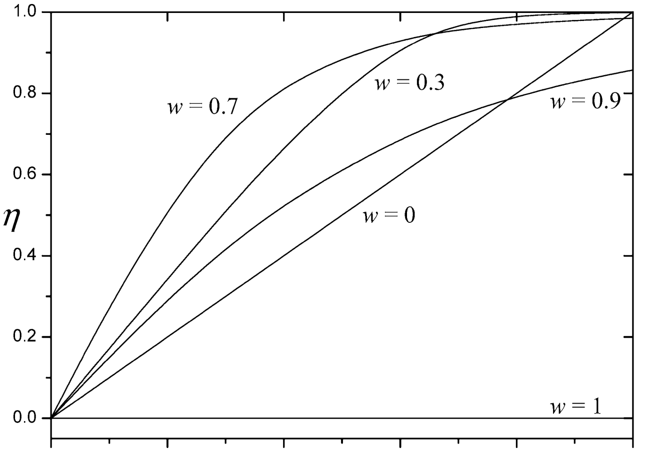

Figure 3. As in Figure 1, at a fixed value of the free energy of a helix reversal of 3.5 k_BT, corresponding to $\sigma = 10^{-3}$.

zero to unity causes a monotonic decrease of the maximum net helicity. Two limiting cases present themselves: $w \to 0$ and $w \to 1$. In the first case, where the mismatch penalty w goes to zero, $\eta \to x$. This in fact holds for all values of σ, as can be seen from eqs 8 and 9. The reason is that for $w = 0$ every "+" monomer must be followed by a "+" bond and every "−" monomer by a "−" bond. The σ independence of the chirality amplification in this limit arises because our model does not allow for a helix reversal without a mismatch free energy being involved. In the second limit, $w \to 1$, the net helicity stays equal to zero over the entire range of x (and σ) values. There is then no longer a penalty on a mismatch between monomer and bond, and the chain conformation will be determined by entropy, leading to a state where half of the bonds have a "+" conformation and half a "−" conformation.

In Figure 3, we plot the net helicity as a function of the enantiomeric excess at a fixed helix reversal penalty of 3.5 k_BT, and we find that the chirality amplification changes in a strongly nonlinear way with w for $\sigma \ll 1$. Strong chirality amplification occurs at values of w around 0.7 (corresponding to an energy penalty of 0.4 k_BT). When the value of w approaches unity, the maximum net helicity decreases, and the value $\eta = 1$ is no longer reached, not even in the case of aggregates that consist of only one type of enantiomer. This means that care must be taken in the interpretation of experimental data, as the maximum obtained optical effect may not correspond to the state in which all bonds are of one type.

In the limit of infinite cooperativity ($\sigma \to 0$) we find from eqs 8 and 9 that η can only have two values, −1 or 1, dependent on whether z and w are smaller or larger than unity. This is because in this limit

$$\eta \to \frac{(w-1)(z-1)}{\sqrt{(w-1)^2(z-1)^2}} \tag{11}$$

The numerator and denominator are identical, albeit that the sign of η varies with w and z. In other words, the aggregates are either fully right-handed or fully left-handed helical for all values of x. This may correspond to the discontinuous phase transition in the one-dimensional Ising model, which occurs under the same circumstances of infinite coupling constant and infinite chain length.

V. Conclusions and Outlook

We present an analytical treatment of the majority-rules type of chirality amplification in solutions of helical, self-assembled polymers, valid in the long-chain limit and exact in the infinite-chain limit. Our treatment requires two free-energy penalties: one on a helix reversal and one on a mismatch between a bond and the monomers near to it. We find that the chirality amplification becomes monotonically stronger with an increasing penalty on a helix reversal but that it shows a strongly nonmonotonic dependence on the mismatch penalty. Finally, we note that for low values of the mismatch penalty fully right-handed or left-handed aggregates no longer form (at least in the regime of infinite chains which we consider here).

Ideally, we would like to compare our theoretical results to experimental ones. Unfortunately, to our knowledge, no measurements have been published on mixtures of enantiomers in self-assembled polymers, and we cannot make a quantitative comparison at this time. Recently, however, preliminary majority-rules experiments have been conducted on self-assembled aggregates of discotic molecules by Palmans and coworkers.[13] Results obtained indicate that our treatment can indeed describe the data, where we find values of the parameters σ and w of approximately 10^{-3} and 0.7. The former corresponds roughly to a degree of cooperativity found in the sergeants-and-soldiers experiment in a similar type of system.[7]

Note that experimental results have indeed been published on the majority-rules principle in helical polyisocyanate copolymers.[4] Although our model does not formally apply to conventional polymers (as mentioned in section I), we tentatively compare our results to these experimental results. We obtain good agreement for $\sigma = 5 \times 10^{-6}$ and $w = 0.91$ (results not shown). We speculate that this means that the discotic monomers form helix reversals more readily than the polyisocyanates do but that they have a somewhat higher mismatch penalty than the conventional copolymers. The good agreement we observe between our theory and both sets of experimental results seems to indicate that equilibrium and fixed disorder give similar results for the majority-rules case.

While our treatment seems to describe known experimental results well, we must nevertheless remember that it is only valid for the long-chain limit. This implies[7] that it can only be sensibly used to describe measurements performed in the concentration-independent regime. If one wishes to describe concentration dependence, an elaboration of our treatment is necessary, analogous to the one given in ref 8 to the ground-state treatment of the sergeants-and-soldiers case. This means that one should retain both eigenvalues of the transfer matrix and use the definitions eqs 6 and 7 to determine the chirality amplification.

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References and Notes

(1) Teramoto, A. *Prog. Polym. Sci.* **2001**, *26*, 667.

(2) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138.
(3) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Wilson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452.
(4) Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H.; Hoke, S.; Cooks, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 4181.
(5) Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Incl. Phenom. Macrocycl. Chem.* **2001**, *41* , 61.
(6) Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Commun.* **2000**, 2305.
(7) van Gestel, J.; van der Schoot, P.; Michels, M. A. J. *Macromolecules* **2003**, *36*, 6668.
(8) van Gestel, J.; van der Schoot, P.; Michels, M. A. J. *J. Chem. Phys.*, in press.
(9) Selinger, J. V.; Selinger, R. L. B. *Phys. Rev. Lett.* **1996**, *76*, 58.
(10) Lee, F. T.; Montroll, E. W.; Yu, L. *J. Stat. Phys.* **1973**, *8*, 309.
(11) Goldenfeld, N. *Lectures on Phase Transitions and the Renormalization Group*, 1st ed.; Addison-Wesley: Amsterdam, 1992; p 88.
(12) Van der Schoot, P.; Michels, M. A. J.; Brunsveld, L.; Sijbesma, R. P.; Ramzi, A. *Langmuir* **2000**, *16*, 10076.
(13) Palmans, A. R. A.; et al., to be published.

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