

Amplification of Chirality of the Majority-Rules Type in Helical Supramolecular Polymers: The Impact of the Presence of Achiral Monomers

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We present a theoretical treatment describing the conformational state of helical supramolecular polymers that consist of three types of monomer: right-handed and left-handed chiral monomers and achiral ones. We find that chirality amplification of the majority-rules type, that is, a disproportionately large shift in the helix screw sense due to a small enantiomeric excess, can occur in these polymers. The strength of the chirality amplification depends on the free-energy penalty of a helix reversal along the self-assembled chain and on that of a mismatch between the conformation of a bond and the preferred conformation of the preceding monomer. It turns out that the impact of achiral monomers also depends on these two parameters. For high values of these free energies, the net helicity does not change much from the situation where no achiral material is present. However, if the free-energy penalties are not both large, the impact of the achiral monomers on the conformational state of the aggregates can be quite substantial.

I. Introduction

The handedness of helical polymers is strongly dependent on the chiral character of their building blocks. Helical polymers (and by extension helical supramolecular aggregates) that consist of achiral monomers exhibit no bias toward either helical twist sense and, hence, display no net optical activity.^{1,2} Polymers constructed from homochiral monomers, on the other hand, do show a bias toward one of the screw senses. This causes a net optical effect that can be measured, e.g., by circular-dichroism spectroscopy.^{3,4}

It is well-known that helical copolymers that consist of homochiral and achiral building blocks can exhibit a highly nonlinear relationship between the net optical effect and the fraction of chiral building blocks; i.e., the chiral monomers can have a disproportionately large effect on the handedness of the polymer (the net helicity). This phenomenon is known as amplification of chirality,^{1,2,5–7} and it is also encountered in helical copolymers comprised of both enantiomers of a chiral monomer. In the former case, the phenomenon is referred to as the “sergeants and soldiers” principle,⁴ whereas the latter case is known as “majority rules”.⁸ Both types of chirality amplification have recently been studied experimentally,^{1–4,6,8–13} as well as theoretically,^{1,3,14–20} and are found to occur both in covalently bound polymers^{1,6–8,10,11,13} and in supramolecular (i.e., self-assembled) ones.^{3,4,9,12}

Recently, there has been some interest in the conformational state of polyisocyanate terpolymers that potentially possess both types of chirality amplification.^{21,22} These polymers consist of both enantiomers, as well as achiral monomers. As far as we know, this type of chirality amplification, called “diluted majority rules”,²² has not yet been studied for self-assembled structures, neither experimentally nor theoretically. In the current paper, we use statistical-mechanical techniques to describe this phenomenon for helical supramolecular polymers. To this end,

we extend our earlier model for the majority-rules principle in this type of aggregate to include achiral monomers.²⁰

Note, however, that our model is not the first theoretical treatment of chirality amplification of the diluted majority-rules type. Indeed, Selinger and Selinger have used a random-field Ising model to describe the conformational state of polyisocyanate terpolymers.²¹ Unfortunately, their theory cannot be directly applied to self-assembled systems. This is because the distribution of the three monomer types is different for supramolecular systems than it is for conventional polymers. In the former type of polymer, the monomer distribution is controlled by the thermodynamic equilibrium, whereas in the latter type, it is fixed a priori, and only the nature of the bonds between the monomers can change. In the problem of chirality induction through the reversible adsorption of chiral molecules onto achiral helical polymers, on the other hand, the distribution of chiral centers is not fixed.^{23,24} In the current paper we apply a theoretical treatment that takes the same form as those used by the authors of refs 23 and 24 in the description of this type of chirality induction, to describe the same phenomenon in a different system, i.e., a solution of helical supramolecular polymers.

This paper is structured as follows. In section II we outline our model for the “diluted majority rules” type of chirality amplification in dilute solutions of long, self-assembled helical aggregates. We determine the relevant partition function and give expressions for the net helicity and the fractions of each type of monomer. In section III we present the results of this procedure, showing that chirality amplification can indeed occur in these solutions and that its strength depends on the value of the free-energy penalty of a helix reversal, on that of a mismatch between the conformation of a bond and the preferred conformation of the monomer that precedes it, and on the fraction of achiral monomers. We find that if both free-energy penalties are large enough, the presence of achiral material has little effect. Conversely, if the free energy of a helix reversal, or that of a mismatch, is small, the achiral monomers may have a larger

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impact, and the net helicity can decrease strongly with an increasing fraction of achiral material. We close the section with a short discussion of our model in the context of earlier work, on both supramolecular aggregates of disklike molecules and polyisocyanate terpolymers. Finally, in section IV, we present our conclusions.

II. Theory

The model detailed below describes the conformational state of self-assembled aggregates containing three types of monomer held together by two types of bond. We restrict ourselves to the description of dilute solutions of long, rigid aggregates, ignoring finite-size effects, as well as interchain and intrachain interactions (that can occur, e.g., through the aggregate folding back on itself). We presume that the chirality amplification is mainly due to short-range interactions, so that we can rely on a one-dimensional multicomponent Ising model²⁵ with nearest-neighbor interactions to properly describe the conformation of the aggregates.^{18,20,26} For the problem at hand, we consider two types of association, one that corresponds to a bond with a right-handed helical screw sense and one that corresponds to a left-handed helical bond, and three types of monomer: achiral monomers that do not bias the helix screw sense, chiral ones that prefer to exist inside a right-handed helix (hereafter referred to as “+” monomers), and chiral ones that have a preference for a left-handed screw sense (the “−” monomers). We reasonably assume that the effects of the latter two monomer types are symmetrical and that the bias induced by a “+” monomer is identical in magnitude to that of a “−” one, albeit opposite in sign.²⁰

To describe the chirality amplification, we define two free-energy parameters: one for the interaction of the monomers with the bonds, and one for the interaction between the bonds themselves. The first of these parameters is the mismatch penalty M , which is invoked whenever a left-handed bond follows a “+” monomer or a right-handed bond follows a “−” monomer. The other is the helix reversal penalty R , and it is applied whenever a right-handed helical bond follows a left-handed one, or vice versa. In other words, it penalizes the occurrence of a “frustrated” monomer, which possesses neither a conformation that corresponds to a right-handed helical bond nor one that corresponds to a left-handed one.²⁰ These energies, and all others used in this paper, are given in units of thermal energy, $k_B T$.

The model described above can be captured in the following dimensionless Hamiltonian for an aggregate of degree of polymerization N .

$$H = \frac{1}{2} R \sum_{i=2}^{N-1} (1 - s_i s_{i-1}) + \frac{1}{2} P \sum_{i=1}^{N-1} (s_i + 1) + \frac{1}{2} M \sum_{i=1}^{N-1} n_i^2 (1 - s_i n_i) + E(N-1) \quad (1)$$

Here, E is the reference interaction free energy that we apply for every bond in the aggregate, and P is the excess free energy of a right-handed helical bond over a left-handed one. We shall set the latter parameter equal to zero below but choose not to do so at this time, for reasons to become clear. In eq 1, s_i gives the state of the i th bond, with $s_i = -1$ for a left-handed helical bond and $s_i = 1$ for a right-handed helical bond; n_i , similarly, gives the nature of the i th monomer, defined to immediately precede the i th bond. Here, $n_i = -1$ corresponds to a “−” monomer, $n_i = 0$ to an achiral monomer, and $n_i = 1$ to a “+” one. Equation 1 is only valid for $N > 2$, but because this is the

regime of interest to us, we need not specify the Hamiltonian for monomers and dimers.

The quasi grand canonical partition function of an aggregate of degree of polymerization N equals

$$\Xi(N) = \prod_{j=1}^N \sum_{n_j=\pm 1,0} \exp \left\{ \frac{1}{2} \mu_-' \sum_{i=1}^N n_i (n_i - 1) + \frac{1}{2} \mu_+' \sum_{i=1}^N n_i (1 + n_i) + \mu_0' \left[N - \frac{1}{2} \sum_{i=1}^N n_i (1 + n_i) - \frac{1}{2} \sum_{i=1}^N n_i (n_i - 1) \right] \right\} \prod_{k=1}^{N-1} \sum_{s_k=\pm 1} \exp(-H) \quad (2)$$

Here, the chemical potentials are defined as follows: μ_0' is the chemical potential of the achiral monomers, μ_-' that of the “−” ones and μ_+' that of the “+” ones. The combinations of a summation symbol and a multiplication symbol that occur in eq 2 indicate repeated sums. The evaluation of this partition function is simplified by the application of the well-known transfer matrix method.^{27–29} This entails that we define a matrix containing the statistical weights of each type of bond, dependent on the bond preceding it. From the eigenvalues of the matrix, the partition function is then readily obtained. For the problem at hand, we need to define three matrixes, one for each monomer type. In case the bond we consider is preceded by an achiral monomer, the matrix becomes¹⁸

$$\mathbf{M}_0 = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma s} & s \end{pmatrix} \quad (3)$$

with $s \equiv \exp(-P)$ the Boltzmann weight for a helical bond, and $\sigma \equiv \exp(-2R)$ the square of the Boltzmann weight of a helix reversal. For a bond following a “+” monomer, it equals

$$\mathbf{M}_+ = \begin{pmatrix} w & \sqrt{\sigma w} \\ \sqrt{\sigma s} & s \end{pmatrix} \quad (4)$$

Here, $w \equiv \exp(-M)$ is the Boltzmann weight for a mismatch between monomer and bond. Finally, for a bond following a “−” monomer, we obtain

$$\mathbf{M}_- = \begin{pmatrix} 1 & \sqrt{\sigma} \\ \sqrt{\sigma s w} & s w \end{pmatrix} \quad (5)$$

To write down the overall transfer matrix, we need to add the elements of these three matrixes, weighed by the fugacity of the corresponding monomer. For this, it turns out to be convenient to renormalize the chemical potentials defined above. We define a reference chemical potential μ_0 that is coupled to all monomers in a chain, and two excess chemical potentials, $\mu_+ = \mu_+' - \mu_0$ and $\mu_- = \mu_-' - \mu_0$. The latter terms give us two fugacities, $z_+ \equiv \exp \mu_+$ and $z_- \equiv \exp \mu_-$. We obtain for the total transfer matrix^{18,20}

$$\mathbf{M} = \mathbf{M}_0 + z_+ \mathbf{M}_+ + z_- \mathbf{M}_- = \begin{pmatrix} 1 + z_- + w z_+ & \sqrt{\sigma}(1 + z_- + w z_+) \\ \sqrt{\sigma s}(1 + w z_- + z_+) & s(1 + w z_- + z_+) \end{pmatrix} \quad (6)$$

The reference fugacity, $z_0 \equiv \exp \mu_0$, and the reference bond free energy, E , are reintroduced in the final expression for the partition function, given below in eq 8.

For the case where only one enantiomer is present in addition to achiral monomers, the matrix (eq 6) reduces exactly to that for the sergeants-and-soldiers principle. We can demonstrate this by setting the fugacity of the monomer that is absent, z_- , equal to zero. If we subsequently set the mismatch penalty

rigidly to infinity ($w = 0$), we obtain the same matrix that we applied in previous work on the sergeants-and-soldiers problem.¹⁸ Reducing the matrix to that of the (undiluted) majority-rules problem is less straightforward, as it requires some redefinitions of the fugacities. It turns out, however, that for the case where achiral material is absent, a matrix is found that corresponds exactly to the definition of the majority-rules problem we use in this paper: a left-handed helical bond is penalized if it follows a “+” monomer and vice versa.

Note that the transfer matrix of eq 6 implies that the helix reversal penalty is the same for all types of monomers. This is not necessarily true, as it can be speculated that achiral monomers may be better suited to being present in a frustrated state—with a left-handed bond on one side and a right-handed one on the other—than chiral ones. If one wishes to correct for this, the transfer matrix should be modified to read

$$\mathbf{M} = \begin{pmatrix} 1 + z_- + wz_+ & \sqrt{\sigma}(1 + uz_- + uwz_+) \\ \sqrt{\sigma s}(1 + uwz_- + uz_+) & s(1 + wz_- + z_+) \end{pmatrix} \quad (7)$$

where u is the Boltzmann factor accounting for the extra penalty of a helix reversal that occurs at a chiral site. In this way, a new effective σ is defined that depends on the fraction of chiral material. In the current paper, we merely wish to point out this possibility and its potential relevance when a comparison is made with experimental results. In the remainder of the paper, we choose to set u equal to unity, and use the transfer matrix as defined in eq 6.

Applying the transfer matrix method, we find that the partition function equals^{18,20,26,29}

$$\Xi(N) = (x\lambda_1^N + y\lambda_2^N) \exp[-E(N-1) + \mu_0 N] \quad (8)$$

In eq 8, x and y are prefactors dependent on the description of the aggregate ends and λ_1 and λ_2 are the eigenvalues of the matrix \mathbf{M} . They are given by $\lambda_{1,2} = (1 + s + sz_+ + swz_- + wz_+ + z_- \pm \Psi^{1/2})/2$, where the plus sign defines λ_1 , and the minus sign λ_2 , and where Ψ is given by $\Psi = 4\sigma s(1 + wz_- + z_+)(1 + z_- + wz_+) + (1 - s + z_- - swz_- - sz_+ + wz_+)^2$. In the long-chain regime, i.e., the regime where the length of an aggregate far exceeds the distance over which a single chiral monomer can influence the conformation of the chain (a correlation length), we can use a ground-state argument and ignore the smaller of the eigenvalues, λ_2 .^{18,20,26,30} While formally only valid in the infinite-chain limit, we may apply this approximation for finite chains, provided the mean chain length remains large. We now obtain for the partition function^{18,20,26}

$$\Xi(N) \approx x\lambda_1^N \exp[\mu_0 N - E(N-1)] \quad (9)$$

In the long-chain limit, we need not deal explicitly with the self-assembly. This is due to the circumstance that, in this regime, the length distribution of the aggregates is quite sharply peaked around its mean value $\langle N \rangle$. Hence, we may represent the mean degree of polymerization by N .

Given eq 9, we can determine the properties of the self-assembled aggregates. The net helicity, η , is defined as the number of right-handed helical bonds minus the number of left-handed ones and can be calculated as follows^{18,20}

$$\eta = -1 + 2(N-1)^{-1} \frac{\partial \ln \Xi(N)}{\partial \ln s} \sim -1 + 2 \frac{s}{\lambda_1} \frac{\partial \lambda_1}{\partial s} \quad (10)$$

Here we ignore the prefactor x from eq 9, because it contains

end effects and as such does not contribute significantly in the long-chain regime. The net helicity turns out to equal

$$\eta = \frac{(z_- - z_+)(w - 1)}{\sqrt{\Psi}} \quad (11)$$

where we have set $s = 1$ ($P = 0$) by symmetry, as already advertised above. The fractions of “+” and “−” monomers, x_+ and x_- , in turn, equal

$$x_+ = N^{-1} \frac{\partial \ln \Xi(N)}{\partial \ln z_+} \sim \frac{z_+}{\lambda_1} \frac{\partial \lambda_1}{\partial z_+} \quad (12)$$

and

$$x_- = N^{-1} \frac{\partial \ln \Xi(N)}{\partial \ln z_-} \sim \frac{z_-}{\lambda_1} \frac{\partial \lambda_1}{\partial z_-} \quad (13)$$

This gives the explicit results

$$x_+ = \frac{z_+ [\Psi^{1/2}(1+w) + 2\sigma(z_- + w + 2wz_+ + 1 + w^2z_-) + (1-w)^2(z_+ - z_-)]}{\Psi^{1/2}[\Psi^{1/2} + (1+w)(z_+ + z_-) + 2]} \quad (14)$$

and

$$x_- = \frac{z_- [\Psi^{1/2}(1+w) + 2\sigma(z_+ + w + 2wz_- + 1 + w^2z_+) + (1-w)^2(z_- - z_+)]}{\Psi^{1/2}[\Psi^{1/2} + (1+w)(z_+ + z_-) + 2]} \quad (15)$$

Note that these equations can only be expected to represent the overall fractions of “+” and “−” monomers in the solution for the long-chain regime. This is because the fractions of each type of monomer inside a single aggregate and the overall composition of the solution can differ substantially if the aggregates are small. That this is not so when the logarithm of the partition function scales with the degree of polymerization (i.e., in the limit where the ground state approximation applies and the role of end effects and finite-size effects is negligible) can be easily shown. Because we only deal with very long aggregates in this paper, and since we do not distinguish the a priori binding free energies for the three monomer types, x_+ and x_- correspond to overall fractions.

It is now possible to determine the magnitude of the chirality amplification for given fractions of chiral material. For this, we solve the fugacities from eqs 14 and 15, for given values of σ , w , x_+ , and x_- , and insert them into eq 11. The results of this procedure are given in the next section.

III. Results

To study how the presence of achiral monomers influences the conformational properties of the supramolecular polymers, we first reexamine the case of “undiluted” majority-rules-type chirality amplification, i.e., the case where the total fraction of chiral material $r \equiv x_+ + x_- = 1$.²⁰ For this, we define the relative enantiomeric excess that corresponds to a net helicity of one-half, $p^* \equiv (x_+ - x_-)/(x_+ + x_-)|_{\eta=1/2}$. In Figure 1, we can see that the value of p^* depends strongly on those of the parameters $w \equiv \exp(-M)$ and $\sigma \equiv \exp(-2R)$.

Let us first focus on the limiting cases $w = 0$ and $w = 1$. In the former case, each “−” monomer must be followed by a

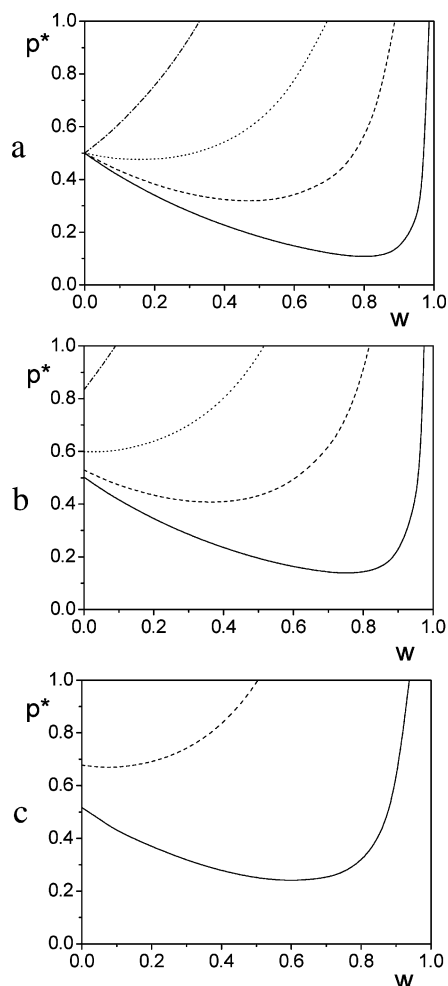


Figure 1. (a) The enantiomeric excess (relative to the fraction of chiral material) necessary to induce a net helicity of one-half, as a function of the mismatch free energy, for several values of the helix reversal penalty, for the case where the fraction of achiral material equals zero. The drawn line corresponds to $\sigma = 0.0001$, the dashed line to $\sigma = 0.01$, the dotted line to $\sigma = 0.1$, and the dash-dot line to $\sigma = 1$. (b) As in part a, but for the case where 40% achiral material is present. (c) As in part a, but for the case where the fraction of achiral material is 0.8.

left-handed helical bond, and each “+” monomer by a right-handed one. Therefore, an enantiomeric excess of one-half yields a net helicity of one-half, independent of the value of the helix reversal penalty. In the limit $w = 1$ we note that a net helicity of one-half is not reached for any of the values of σ . This is because in this limit there is no penalty on a mismatch and therefore no bias toward either screw sense. This means that both twist senses are formed in a 1:1 ratio, and η equals zero. The same result is found if only achiral monomers are present ($r = 0$). This is because in both cases, the monomers become indistinguishable in their (lack of) preference for specific bond types.

In the undiluted majority-rules case, amplification of chirality occurs when the net helicity equals one-half at an enantiomeric excess below one-half. Hence, we can conclude from Figure 1 that for $\sigma = 1$, no chirality amplification occurs. As σ decreases (i.e., as the helix reversal penalty increases), however, chirality amplification does occur, the more so, the lower σ . This is because the cooperativity increases with increasing helix reversal penalty. This manifests itself in an increase in the number of bonds that are influenced by a single “+” monomer, and consequently in the bare correlation length (the mean distance

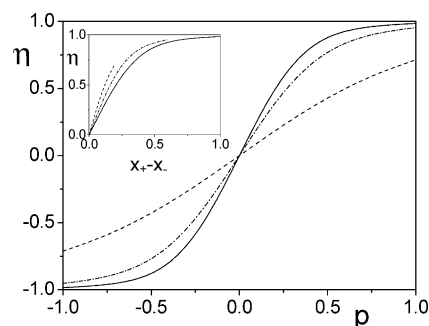


Figure 2. The net helicity versus the relative enantiomeric excess, for $w = 0.7$ and $\sigma = 0.001$, and three values of the fraction of chiral monomers, r . The drawn line corresponds to $r = 1$, the dot-dash line to $r = 0.6$, and the dashed line to $r = 0.2$. Inset: the net helicity as a function of the absolute enantiomeric excess (for clarity, only the right-hand portion of the curve is shown), for three values of the fraction of chiral material. The lines have the same meaning as those in the main figure.

between two helix reversals in the absence of any chiral material, found to equal $1 + \sigma^{-1/2}$).¹⁸ Due to this, the majority-rules effect also increases.

The role of w is less straightforward, as the dependence of the chirality amplification on w is strongly nonlinear and nonmonotonic;²⁰ for low σ , there is first an increase in chirality amplification with increasing w and then a rapid decrease. The initial increase is due to the circumstance that a lower mismatch penalty allows for more of the minority-type monomers to be present inside an aggregate without changing its net helicity, whereas the final decrease can be understood using the same arguments that explain the behavior of the chain for $w = 1$, as detailed above. A maximum in the strength of the chirality amplification can be seen at approximately $w = 0.8$ for the values of σ plotted in Figure 1, shifting to lower values as achiral monomers are added.

Further effects of the presence of achiral monomers can be seen in parts b and c of Figure 1. Generally, achiral material causes a decrease in the net helicity of the polymers at the same (relative) enantiomeric excess. For a mixture in which 40% of the assembling material is achiral (Figure 1b), we see that the value of p^* at $w = 0$ shifts from 0.75 to higher values. In Figure 1c, we even see that the addition of 80% of achiral material means that a net helicity of one-half can no longer be reached for $\sigma = 1$ or $\sigma = 0.1$. The amount by which the value of p^* shifts relative to the undiluted majority-rules case depends on the value of the cooperativity parameter σ (and on that of the mismatch parameter w); a larger value of σ causes a larger shift. This is true not only at $w = 0$ but for all values of w . (See Figure 1). This makes sense, because, as we discussed above, a small value of σ indicates that a chiral center can influence many of the bonds following it, whereas a large value implies that this effect is short-ranged. The presence of achiral monomers also shifts the location of the maximum in the chirality amplification. It shifts to lower values of w and slightly higher values of p^* . The latter shift means that, even at relatively low σ , the chirality amplification still decreases somewhat due to achiral material, whereas the former one implies that a larger penalty on a mismatch is necessary to obtain the maximal value of the net helicity than in the case without any achiral material.

In Figure 2, we take a more detailed look at the chirality amplification for a fixed value of $w = 0.7$ (corresponding to a relatively small mismatch penalty). On the horizontal axis we plot the enantiomeric excess, relative to the fraction of chiral material, $p = (x_+ - x_-)/(x_+ + x_-)$, whereas on the vertical axis

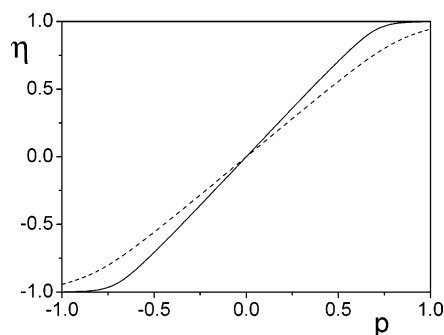


Figure 3. The net helicity versus the enantiomeric excess, relative to the fraction of chiral material, for $w = 0.2$ and $\sigma = 0.001$, and two values of the fraction of chiral monomers, r . The drawn line corresponds to $r = 1$, and the dashed line to $r = 0.2$.

is the net helicity. We find a relatively strong decrease in the net helicity as the fraction of achiral material increases. For the case where 80% achiral material is introduced, we see furthermore that even a total absence of the “−” monomer can no longer induce the formation of an exclusively right-handed helix. This is due to two effects. The first is obviously the presence of the achiral material. As these monomers have no preference for either screw sense, some of them are likely to be followed by left-handed helical bonds (unless the cooperativity becomes very high, $\sigma \rightarrow 0$). The other reason can be found in the value of M . Since it is quite small, this mismatch penalty allows for some left-handed helical bonds to follow “+” monomers. It is the latter contribution that causes the value of η at $p = 1$ to differ from that found in earlier studies of the sergeants-and-soldiers type of chirality amplification. There we had rigidly assumed that a “+” monomer must always be followed by a right-handed helical bond ($w = 0$), and as a result, we found, for the same value of σ , a value of η of approximately 0.95, as opposed to the value of 0.71 we find here.

It seems that, at a fraction of achiral material of 80%, chirality amplification no longer occurs. This, however, is due to our choice of p on the horizontal axis. If we were to use instead the overall enantiomeric excess, $x_+ - x_-$, then we would see that a small (absolute) enantiomeric excess still yields a disproportionately large shift in the net helicity. This is shown in the inset to Figure 2, where we in fact see that the chirality amplification *increases* slightly with added achiral monomers, when plotted in this fashion. This is because achiral monomers more readily accommodate a left-handed (right-handed) helical bond than do “+” (“−”) monomers and, as such, allow for a larger net helicity at the same value of the overall enantiomeric excess.

The effect of a change in the value of the mismatch penalty on the impact of achiral material is shown in Figures 2 and 3. Where, in Figure 2, we saw that relatively high values of w induce a large shift in the net helicity as a function of the relative fraction of “+” monomers, in Figure 3 we observe that for low values of w (high values of the mismatch free energy M) this shift is much smaller, for the same value of the helix reversal penalty. This implies that the strength of the preference of a chiral molecule for a specific type of helical bond can indeed have a large impact on the conformational state of the aggregates.

As far as we are aware, no experiments have been performed on chirality amplification in self-assembling helical structures formed from mixtures of achiral monomers and both enantiomeric forms of the chiral monomers. Hence, a direct comparison to experiment is impossible at this time. However, we can predict the conformational state of one such self-assembling

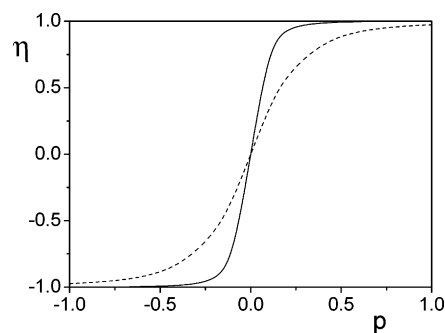


Figure 4. The net helicity versus the relative enantiomeric excess, for $w = 0.91$ and $\sigma = 5 \times 10^{-6}$, corresponding to the values found for chiral polyisocyanate copolymers in ref 20, and two values of the fraction of chiral monomers, r . The drawn line corresponds to $r = 1$, and the dashed line to $r = 0.2$.

system. Recently, we have compared experimental results on the (undiluted) majority-rules-type behavior of discotic molecules in *n*-octane with an earlier theory and found good agreement for values of σ of 1.7×10^{-3} and w of 0.68.¹² We assume that the presence of achiral material does not alter these values. This is reasonable because we have defined the helix reversal penalty to be independent of monomer type and because the mismatch penalty is only applied for chiral monomers, and not for achiral ones. Given this, we can predict how this system reacts to dilution with achiral material. Since the values of σ and w are quite close to those of Figure 2, this figure provides our qualitative prediction: for the discotic molecules in *n*-octane, an increase of the fraction of achiral material (at a fixed relative enantiomeric excess) is likely to have a strong effect on the net helicity. We expect that the optical activity of the solution, measurable by circular-dichroism spectroscopy, shall decrease only slightly if the fraction of achiral material is small but much more strongly if a large amount of achiral material is present in a similar way as shown in Figure 2.

Experimental findings on the diluted majority-rules principle in helical polyisocyanate terpolymers, as well as a theoretical description and simulation results, have been published recently.^{1,21,22} Direct comparison with our theory appears to be impossible, however, not only because our model presupposes a monomer distribution determined by the thermodynamic equilibrium, as opposed to a fixed one, but also because the experiments and simulations were performed in the short-chain regime, while our theory covers only the long-chain regime. The latter circumstance manifests itself (for the experimental results) in the dependence of the optical effect on the polymer length. In the simulations, a polymer length of 200 monomers is applied; this is shorter than the bare correlation length, which equals almost 500 monomers for the value of $\sigma = 5 \times 10^{-6}$ we obtained from a comparison of our earlier theory to majority-rules-type experiments on these polymers.^{8,20} Therefore, these simulations, too, were performed in the short-chain regime, where finite-size effects are important, and their results cannot be reproduced with the current model.

Nevertheless, we can tentatively predict how the optical effect may depend on the fraction of achiral monomers in *long* polyisocyanate terpolymers. For values of $\sigma = 5 \times 10^{-6}$ and $w = 0.91$, which we found described the experimental results for the undiluted majority-rules case best,²⁰ we show the predicted trends in Figure 4. While the value of σ is quite small (and the cooperativity correspondingly high), the large value of w ensures that some decrease in the net helicity is still observed. Our prediction qualitatively matches the simulation results of Selinger and co-workers for short chains. Unexpectedly, the curve

at 80% achiral material even gives a good quantitative agreement (not shown), whereas the curve we find for the undiluted case is somewhat steeper than that of the simulations of ref 21.

A complication that may occur during experimental measurements is that of specific interactions between the different types of monomer. We have assumed that the distribution of the monomers in the aggregate is random. However, it is possible that like monomers attract each other, causing clustering of these monomers to occur. Alternatively, repulsion of like monomers may take place. These effects cannot be taken into account in the current model but require the introduction of monomer–monomer interactions, on top of bond–bond and monomer–bond interactions. Selinger and co-workers examine these effects in their recent paper²¹ and find that the chirality amplification becomes more pronounced if the interaction between like monomers is repulsive and less so if it is attractive. Another phenomenon that may occur in experiment is the appearance of a maximum in the dependence of the optical effect on the fraction of achiral material. This is because the contributions to the optical effect of achiral and chiral monomers may differ, a circumstance discussed in some detail in ref 18, for the sergeants-and-soldiers case.

IV. Conclusions

We outline an analytical theory that describes chirality amplification in long self-assembled polymers comprised of achiral monomers and chiral monomers, in which both enantiomers of the latter are present. It turns out that an increase in the fraction of achiral material causes a decrease in the net helicity at a fixed relative enantiomeric excess. The amount by which the net helicity decreases, when compared to the “undiluted” majority-rules case, depends on the values of the helix reversal free energy and the free energy of a mismatch between the screw sense of a helical bond and the preferred screw sense of the preceding monomer. If both these parameters are large, then the impact of achiral material is modest. Conversely, if either of them is small, dilution with achiral monomers may cause a substantial shift in the net helicity of the aggregates. At a fixed fraction of each type of monomer, a decrease of the helix reversal free energy leads to a decrease in the strength of the chirality amplification. The dependence on the mismatch free energy, on the other hand, is nonmonotonic, and a maximum in the chirality amplification may be observed for a finite value of this parameter.

References and Notes

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- (30) Note that the use of a ground-state argument implies that the theory can only be sensibly applied to describe experimental results for which the chirality amplification is independent of the overall concentration of self-assembling material. A description of a concentration-dependent “diluted majority-rules effect” requires that we take into account chains of any length. The method by which our treatment may be extended to encompass these chains is well-known and involves retaining both eigenvalues of the transfer matrix. See, e.g., ref 19 for a detailed discussion.