Amplification of Chirality in Helical Supramolecular Polymers

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ABSTRACT: We theoretically studied the sergeants-and-soldiers principle of chirality amplification in self-assembled, *supramolecular* helical polymers and show that a mapping is possible on a two-component Ising chain, in which one of the components has a spin of fixed orientation. The relative abundance of this component is regulated by a chemical potential. Our theory quantitatively describes recently published measurements of the optical activity of linear assemblies of certain discotic molecules in solution. We find that the strength of the chirality amplification depends strongly on the strength of the coupling between the spins, which translates into a free-energy penalty put on a helix reversal along the backbone of the self-assembled polymer.

I. Introduction

It is well-known that the handedness of helical homopolymers is determined by chiral centers, present either in the backbone or in side groups. Polymers that contain no chiral centers can be helical too, but by symmetry cannot, in the mean, display a preferred handedness.[1] If sufficiently long, such polymers consist of left-handed and right-handed helical regions of variable length, which are in principle in dynamic equilibrium with each other. The mean length of these regions is determined by the free-energy cost of a helix reversal.[2] The larger this free-energy cost, the larger the (mean) distance between helix reversals.

In this context, it is perhaps not entirely surprising that the copolymerization of a small amount of homochiral monomeric units with achiral material can have a disproportionately large effect on the net handedness of a helical polymer.[1−3] This expresses itself in an optical activity of the polymer that increases highly nonlinearly with the relative amount of homochiral material. Indeed, it is often seen that only a few percent of chiral material is necessary to attain the maximal Cotton effect, a phenomenon usually referred to as the "sergeants-and-soldiers" principle.[4] The chiral monomers (the "sergeants") direct the configuration of the achiral ones (the "soldiers") near to them over a distance that is set by the free-energy penalty of a helix reversal.[5]

The sergeants-and-soldiers principle of copolymers as well as other types of chirality amplification have been the topic of much experimental[1,3,4,6] and theoretical[2,5,7,8] work. The theories, which make use of quite diverse theoretical tools, reproduce available experimental data often quantitatively, and confirm the important role of helix reversals.[2,5] They also show that, in the long-chain limit, chirality amplification becomes independent of the molecular weight of the polymer.[2,7]

Recently, it has become evident that chirality amplification is not restricted to conventional polymers. Meijer and co-workers observed a large sergeants-and-soldiers effect in solutions of *supramolecular* polymers,[9,10] i.e., polymer-like aggregates formed through the linear self-assembly of monomeric units. In our view, this is remarkable, because we would expect the monomer−monomer distance in these relatively weakly bound assemblies to be larger than in conventional polymers and therefore any chiral interaction between them to be weak. In clear contrast to this naive expectation, we observe that the strength of the sergeants-and-soldiers effect in these aggregates is in fact quite high, and comparable to that in some conventional polymers.

Unfortunately, available theoretical methods aimed at describing the sergeants-and-soldiers effect in conventional polymers cannot be applied to supramolecular polymers (at least not in principle). The reason is that in supramolecular polymers the monomeric and polymeric states are in thermodynamic equilibrium, leading to an equilibrium distribution of the chiral and achiral components along the chains, whereas in conventional polymers this distribution is fixed. In this work, we set up a minimal theory that specifically describes chirality amplification of the sergeants-and-soldiers type in helical supramolecular polymers and that is able to deal with this equilibrium distribution of chiral and achiral monomers.

As it turns out, the same physical principles regulate this type of chirality amplification in both types of polymer, provided they are long enough. The advantage of our theory is that it is analytical and exact in the infinite-chain limit, unlike current theories for conventional copolymers that either require input from numerical simulations or involve approximations to describe the chirality amplification. In addition, our theory also allows for a simple determination of the free energy associated with a helix reversal from experimental data.

The experiments of Meijer and co-workers[9,10] point at the existence of two regimes, one where the sergeants-and-soldiers effect is virtually independent of the concentration and one where this is not so. According to the standard theory of linear self-assembly, the mean molecular weight of supramolecular polymers grows with the square root of the concentration.[11] This implies that, in the former regime, the sergeants-and-soldiers effect is independent of the molecular weight and that the long-chain limit applies. For the latter regime, it follows that the sergeants-and-soldiers effect does depend on the mean length of the aggregates and that the self-assembly and chirality amplification are strongly

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coupled. For reasons of simplicity, we focus in this paper on the long-chain limit, where the self-assembly is enslaved by the configurational statistics of the aggregates.[11] The other limit, in which the self-assembly and the configurations of the chains are coupled, requires a much more elaborate theoretical description that we deal with in a separate publication.

The remainder of the paper is structured as follows. In section II, we outline our theory for the amplification of chirality in supramolecular polymers in terms of a one-dimensional, two-component Ising model. We present an implicit expression for the relative difference between the numbers of left- and right-handed helical bonds as a function of the fraction of chiral molecules in the chain and of the free energy of a helix reversal. Next, in section III, we solve this implicit expression numerically and present the results of our calculations. The fraction of chiral material needed to almost completely suppress the handedness incompatible with the structure of the chiral monomers turns out to be roughly equal to the Boltzmann factor associated with a helix reversal. We confront our theory with experimental data of mixtures of chiral and achiral discotic molecules in water, obtained by means of circular-dichroism spectroscopy.[9] For comparison, we also fit our theory to optical-activity measurements on solutions of a conventional polymer.[4,5] In both cases, we get excellent agreement, although our theory should not hold for conventional polymers. Finally, we present our conclusions in section IV.

II. Theory

We consider a dilute solution of helical supramolecular polymers, allowing us to disregard interaggregate interactions. The aggregates are thought to be sufficiently rigid to make long-range intra-aggregate interactions such as those of the excluded-volume type unimportant. They consist of two types of monomer, one chiral and one achiral. Presuming the direct interactions of monomers along the chain to be short-ranged, we can rely on a one-dimensional, two-component Ising model[12] to accurately describe the conformational properties of these aggregates. Note that similar models have been applied in the past to describe amplification of chirality in conventional polymers.[2,5,7] As we already briefly discussed in the Introduction, the difference with the earlier work is that for a supramolecular polymer the distribution of the two components over the one-dimensional lattice is not fixed, but is an equilibrium property. While the configurations of both types of polymer can (if only in principle) be described with the same model Hamiltonian, the methods of calculation of various average quantities are different.[13]

The model we use bears a close resemblance to mixed one-dimensional lattice fluids with Ising interactions.[14−16] In the work of Leung and co-workers[14] and that of Chiang and co-workers,[16] both components can take the spin values ±1. In the work of Kawatra and co-workers,[15] one component is spinless, while the other can again take the spin values ±1. In contrast, the sergeants-and-soldiers experiment is most naturally described by letting one of the components have a spin of a fixed value equal to either +1 or to −1, and letting the other take both the values ±1.

Let us for simplicity first deal with helical aggregates consisting only of achiral monomers, which we can treat with the simple (slightly modified) one-component Ising model. (Later on we introduce the second, chiral, component that acts like an instantaneous, localized magnetic field to which the first component couples.) In our description, we assign a spin of +1 to a helical bond of one handedness and a spin of −1 to one of the opposite handedness. For reasons to become clear below, we impose an external magnetic field that couples to the spins and shifts the balance between the "up" and "down" spins. Obviously, in zero magnetic field, both spins are equally probable, irrespective of any (finite) coupling between them.[13]

The dimensionless Hamiltonian of the model of an aggregate consisting of N monomers (linked by $N - 1$ bonds) reads

$$H = \frac{1}{2}R\sum_{j=1}^{N-2}(-s_j s_{j+1} + 1) + \frac{1}{2}P\sum_{j=1}^{N-1}(s_j + 1) - E(N - 1) \tag{1}$$

Here, $R \geq 0$ is the usual coupling constant between neighboring spins, representing the free-energy penalty on a helix reversal. P is the dimensionless magnetic-field strength, and corresponds to the excess free energy associated with a bond of one handedness over the other. The free energy of the reference bond we set equal to $-E$. The prefactors of one-half in front of the first two terms in eq 1 are present to avoid the double counting of the contributions of the "up" spins and that of the interfaces between "up" and "down" spins. The Hamiltonian is given in units $k_B T$, as are all energies in this paper.

From the Hamiltonian in eq 1, we determine the (canonical) partition function $Q(N)$ of an aggregate. This can be done exactly with the well-known transfer-matrix method.[17] In the large-aggregate regime, $N \gg 1$, $Q(N)$ can be simplified considerably by applying the so-called ground-state approximation, which retains only the largest eigenvalue of the transfer matrix. This gives[11,18]

$$Q(N) = \sum_{s_1=\pm1}\cdots\sum_{s_{N-1}=\pm1}\exp(-H) \approx A(s,\sigma)\lambda^N \exp E(N-1) \tag{2}$$

with $A(s,\sigma)$ a prefactor that we need not specify, containing contributions that are nonextensive in the aggregate size and that depend on the boundary conditions.[19] In eq 2, $\lambda = {}^1/_2 + {}^1/_2 s + {}^1/_2\sqrt{(s-1)^2+4\sigma s}$ is the largest eigenvalue of the transfer matrix with $s \equiv \exp -P$ the Boltzmann factor of an "up" spin and $\sigma \equiv \exp -2R$ the square of the Boltzmann factor of a helix (or spin) reversal. The latter functions as a cooperativity parameter: the smaller σ, the larger (in effect) the distance over which spins influence each other and the sharper the magnetization curve. The mean distance between helix reversals (a correlation length) is given by $N(1 - \partial(\ln Q)/\partial R)^{-1}$and can be calculated from eq 2. Here the derivative $-\partial(\ln Q)/\partial R$ gives the number of helix reversals, so that the number of regions into which the helix reversals divide the aggregate is $1 - \partial(\ln Q)/\partial R$.

Note that by symmetry, the relevant case for a polymer consisting solely of achiral monomers is that where $s = 1$, since achiral monomers have no preference for either helical handedness. For this value and in the limit $N \gg \sigma^{-1/2}$, the distance between helix reversals is equal to $1 + \sigma^{-1/2}$, as follows by simple insertion.[18] It is easily seen that the distance between helix inversions becomes large for small σ.

Formally, the ground-state result of eq 2 is valid only for $N \gg 1$ (and exact in the limit $N \to \infty$), but it may be extrapolated down to $N > 2$. This is sensible as long as the mean aggregate size, $\langle N\rangle \simeq \sqrt{\phi A^{-1}(s,\sigma)\exp E}$, obtainable by inserting eq 2 into the standard theory of linear self-assembly, remains large.[11] Here, ϕ is the volume fraction of aggregating molecules and $E - \ln A(s,\sigma)$ assumes the role of an energy associated with two aggregate ends (the so-called end-cap energy). See, e.g., ref 11 for a discussion of this energy. The prefactor $A(1,\sigma)$ for $s = 1$ becomes a constant equal to 2 if both aggregate ends are free to assume a right- or left-handed conformation.[19] Since in the long-chain limit the mass distribution of the aggregates is peaked around $N = \langle N\rangle$, we need not explicitly deal with the self-assembly. Hence, from now on we imply the aggregation number N to represent its (concentration and temperature dependent) mean value $\langle N\rangle$.

To obtain the net magnetization (or net helicity, which we define as the difference between the fractions of right- and left-handed helical bonds), we first calculate the fraction of "up" spins, $\theta_+ = -N^{-1}\partial(\ln Q)/\partial P$. We find

$$\theta_+ = 1 - \theta_- = \frac{1}{2} + \frac{s-1}{2\sqrt{(s-1)^2 + 4s\sigma}} \tag{3}$$

independent of $\langle N\rangle \gg 1$, with θ_- the fraction of "down" spins. The net magnetization per site η (or the net helicity per bond) is a measurable quantity (at least in principle) and is defined as the difference between the fractions of "up" and "down" spins

$$\eta \equiv \theta_+ - \theta_- = 2\theta_+ - 1 \tag{4}$$

Obviously, for our achiral polymers, $s = 1$ so $\eta = 0$; η can only become larger than zero if we add chiral material.

We now consider the case that there are two types of monomer present, chiral and achiral. This changes the above equations in a number of ways. First, based on the idea that chiral monomers have a distinct preference for a certain handedness and achiral ones do not, we arbitrarily define that a chiral monomer is always followed by an "up" spin, whereas an achiral monomer can be followed by either spin. Obviously, the free energy of a "down" spin following a chiral monomer can also have a finite value, rather than the infinite value we impose in our description. We choose to forbid such a "mismatch" configuration in order to avoid having to introduce another parameter in our model, thus keeping the number of model parameters to a bare minimum. In the Results and Discussion section, we discuss the impact of a finite free-energy penalty in some detail.

The dimensionless Hamiltonian H' for the copolymer becomes

$$H' = \frac{1}{4}R\sum_{j=1}^{N-2}\left(-\frac{n_j+1}{s_j+n_j}\frac{n_{j+1}+1}{s_{j+1}+n_{j+1}} + 1\right)^2 + \frac{1}{2}P\sum_{j=1}^{N-1}\left(\frac{n_j+1}{s_j+n_j} + 1\right) - E(N-1) \tag{5}$$

where $n_j = 1$ corresponds to a chiral particle, and $n_j = 0$ to an achiral one. It is easily checked that for an achiral aggregate, for which $n_j = 0$ for all j, eq 5 reduces to eq 1, because the equalities $s_j^{-1} = s_j$ and $s_j^2 = 1$ hold in our case. Here, we have assumed that the interaction parameters R and P (and therefore also the corresponding free energies) are identical for bonds following chiral and achiral molecules. Note that our Hamiltonian H' is constructed such that all configurations in which a "down" spin follows a chiral monomer are completely suppressed, giving a Boltzmann weight that is exactly zero.

Because the composition of an aggregate of N molecules can vary, it makes sense to invoke a quasi-grand canonical ensemble rather than the canonical ensemble we used for the single-component aggregate. The associated quasi-grand partition function $\Xi(N)$ can be written as

$$\Xi(N) = \sum_{s_1=\pm1} \cdots \sum_{s_{N-1}=\pm1}\sum_{n_1=0,1} \cdots \sum_{n_N=0,1} \exp(-H' + \mu\sum_{j=1}^{N} n_j) \tag{6}$$

Here, μ is a dimensionless excess chemical potential of the chiral component. Despite the apparent difference between the canonical and quasi-grand canonical partition functions, eqs 2 and 6, $\Xi(N)$ can be written in the same form as the earlier discussed $Q(N)$. We only have to replace the Boltzmann factor s by an appropriately modified one, s', due to the presence of the chiral component. Using the Hamiltonian in eq 5, we can formally derive an expression for this modified Boltzmann factor with the aid of the transfer-matrix method, giving exactly $s' = s(1 + \exp\mu)$, where s retains its previous meaning as the Boltzmann factor of an "up" spin over a "down" spin.

That we merely need to replace s by $s(1 + \exp\mu)$ can also be seen from the following simple probability considerations. One has to realize that the quantity s' may be seen as the (unnormalized) probability that a randomly chosen spin along the chain is in an "up" conformation. For the mixed system, this probability is equal to the sum of the probability of an "up" conformation following a chiral monomer (which occurs with a probability dependent on its chemical potential), and that of an "up" conformation following an achiral monomer.[20] From this, the total unnormalized probability for a random spin to have an "up" configuration must indeed be $s' = s(1 + \exp\mu)$.

We now impose, as discussed earlier, the condition that achiral molecules should have no preference for spin "up" or spin "down", by putting $s = 1$ (or $P = 0$). In other words, $s' = 1 + z$ with $z \equiv \exp\mu$ a fugacity that determines the fraction chiral monomers in the chain. Replacing s by s' in eqs 3 and 4, we conclude that the net magnetization per site must equal

$$\eta = \frac{z}{\sqrt{z^2 + 4(z+1)\sigma}} \tag{7}$$

For aggregates composed entirely of achiral monomers, $z \to 0$ so $\eta \to 0$; "up" and "down" conformations are then equally likely. For fully chiral aggregates, $z \to \infty$ and $\eta \to 1$. In the ground-state approximation, the mean aggregate size $\langle N\rangle$ is enslaved by quantities such as z and η that describe the conformational state, and is only very weakly dependent on them. In this case the conformational transition and the aggregate growth are virtually independent, so we need not discuss this issue any further.

The fraction of chiral material in the aggregates, x, can be calculated directly from eq 6. From standard statistical mechanics we know that $x = N^{-1}\partial(\ln\Xi(N))/\partial\mu$. This gives

$$x = \frac{(\eta + 1)z}{2(1 + z)} \tag{8}$$

which is exact in the limit of infinite aggregates. Substituting eq 7 into eq 8, we deduce that x can be expressed as a function only of z and σ. We can eliminate z, and obtain an implicit expression for η as a function of x,

$$x = (\eta + 1)\frac{\sigma\eta^2 + \eta^2\sqrt{\sigma\eta^{-2} + \sigma^2 - \sigma}}{1 - \eta^2 + 2\sigma\eta^2 + 2\eta^2\sqrt{\sigma\eta^{-2} + \sigma^2 - \sigma}} \tag{9}$$

It turns out to be useful to define a quantity x_* as the fraction chiral material needed to induce one-half of the maximum attainable helicity, $\eta = {}^1/_2$. From eq 9, we find that

$$x_* = \frac{3}{2}\frac{\sigma + \sqrt{3\sigma + \sigma^2}}{3 + 2\sigma + 2\sqrt{3\sigma + \sigma^2}} \approx \frac{1}{2}\sqrt{3\sigma} \tag{10}$$

for $\sigma \ll 1$. Equation 10 provides an convenient way to directly obtain the free energy of a helix reversal from experiment.

In experiment one measures an optical effect that depends on the total amount of helical material in a probe volume. This in turn depends, e.g., on the optical path length, the concentration of dissolved material, and the optical properties of the molecules. To account for this we introduce a constant of proportionality α that links the theoretical and experimental optical effects. Furthermore, the contributions to the optical effect from the two types of monomer in a helical aggregate may be unequal in magnitude, and we also need to account for that. We do this by defining the ratio γ between these contributions for a chiral and an achiral monomer and assigning this weight to each bond that follows a chiral monomer, the fraction of which is $z(z + 1)^{-1}$. The fraction of bonds that follow an achiral monomer equals $(z + 1)^{-1}$, and to these we assign the weight 1. The measured net helicity denoted by η' is thus in our description given by a linear superposition of the two weights and may be expressed as

$$\eta' = \alpha\eta\left[1 + (\gamma - 1)\frac{z}{z + 1}\right] \tag{11}$$

The roles of σ and γ are discussed in the next section, where we also make a comparison to experimental data.

III. Results and Discussion

To illustrate how cooperativity influences the amount of chiral material needed to (almost) completely suppress left- or right-handed helical configurations in initially achiral supramolecular chains, we have plotted eq 11 in Figure 1 for $\alpha = \gamma = 1$. It clearly shows that the smaller σ, the less chiral material is needed to achieve the same net helicity. This can in fact also be deduced directly from eq 10 that gives x_* as a function of σ. Note that in the limit $\sigma \to 1$ there is no amplification of chirality, and chiral and achiral monomers behave as a simple mixture with $\eta = x$.

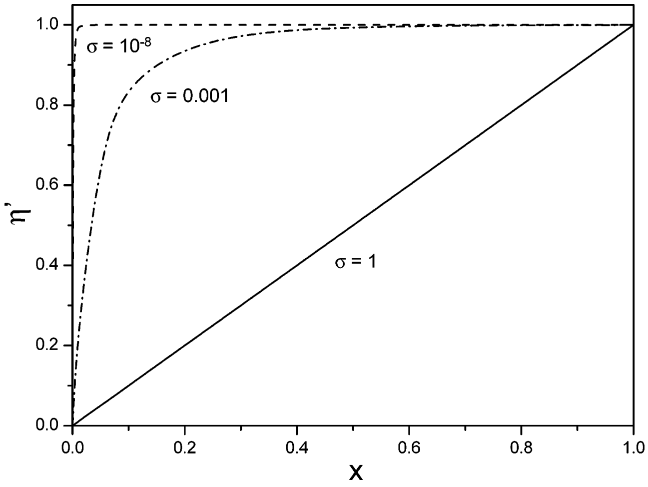

Figure 1. Net helicity η' as a function of the fraction of chiral material x, for $\alpha = \gamma = 1$ and three values of the cooperativity parameter: $\sigma = 1$ (solid line), $\sigma = 10^{-3}$ (dot−dash line), and $\sigma = 10^{-8}$ (dashed line).

Note further that, in our model, a fully chiral aggregate cannot exhibit helix reversals, so $\eta \to 1$ for $x \to 1$ for all values of σ. This, obviously, is an approximation. To allow for mismatches, i.e., configurations in which a "down" spin follows a chiral monomer, we can include a finite free-energy penalty U. If we do this, however, we find that $\sigma \to \sigma/(1 - u)^2$, with $u = \exp -U$, the Boltzmann weight of the mismatch energy, at least for conditions where U exceeds the helix reversal penalty, and $\sigma \ll 1$ (this being the limit most interesting from an experimental perspective). In other words, the mismatch energy only renormalizes the helix reversal free energy in this case. This means that the value of σ that we obtain from fits to experiment is the actual value of $\exp -2R$ only if $u \ll 1$, and an effective one otherwise. It does not seem possible to disentangle u and σ experimentally, and obtain the actual σ from the effective one. However, if we estimate that $-U$ is on the order of the bond energy (which is typically $10-20k_BT$ for this type of system[11]), u is indeed much smaller than unity, and the value of σ we obtain will be close to the actual helix reversal penalty.

The effect of the optical parameter γ on the net helicity is shown in Figure 2, for the case where $\alpha = 1$. While for low fractions of chiral material η' is insensitive to γ, for high fractions it displays a maximum if $\gamma < 1$. This is because chiral molecules have a lower contribution to the overall optical effect than do achiral ones if $\gamma < 1$. At fixed α, a further decrease of γ decreases the height of this maximum and moves it to lower x. For $\gamma > 1$ (when chiral molecules have a larger contribution to the optical signal than achiral ones) the curve continues to rise, even when the bare helicity has saturated at $x < 1$. This could lead to difficulties if interpreting experimental results, since one could erroneously draw the conclusion that the maximum helicity has not yet been reached, when in fact it has. Note that the approximate eq 10 can still be used to fix the cooperativity parameter σ even if $\gamma \neq 1$, since x_* is insensitive to the precise value of γ if the cooperativity is sufficiently large.

We now confront the prediction of our theory with experimental data[9] on a certain type of discotic molecule that for brevity we refer to as "C_3 discotic", dissolved in water. These molecules have a molecular weight of about 3400 and consist of aromatic cores, surrounded

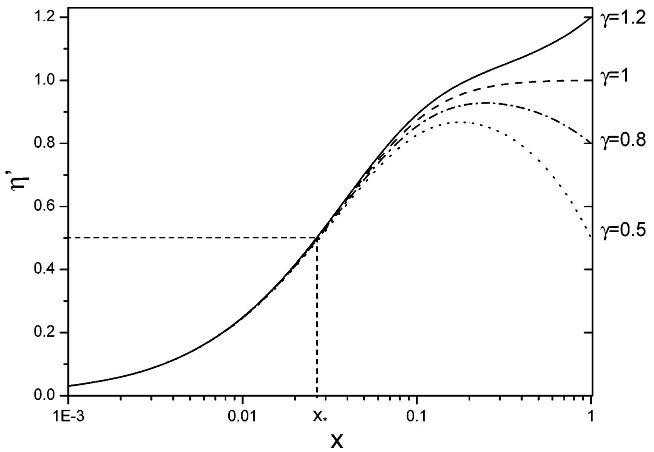

Figure 2. Net helicity η' as a function of the fraction of chiral material x at $\sigma = 10^{-3}$, for four values of the ratio between the contributions to the helicity of the chiral and achiral components γ. The solid line gives $\gamma = 1.2$, the dashed line $\gamma = 1$, the dot−dash line $\gamma = 0.8$, and the dotted line $\gamma = 0.5$. The fraction chiral material giving a net helicity of half its maximum value x_* is indicated for $\gamma = 1$.

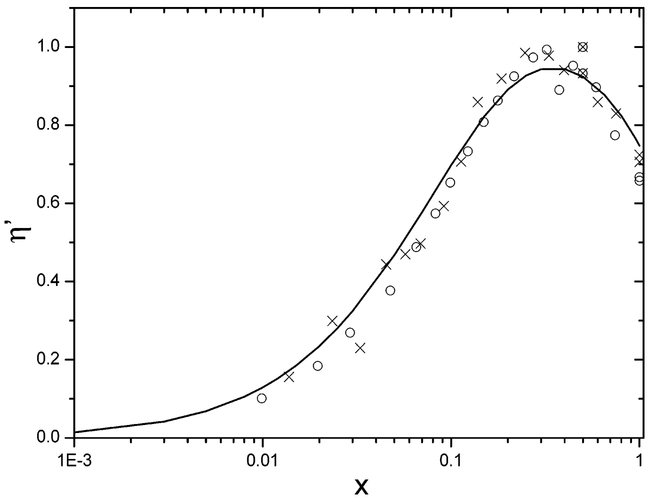

Figure 3. Net helicity η' vs the fraction of chiral material x (line). Symbols: experimental data of Brunsveld et al. at two concentrations (circles, 10^{-5} M; crosses, 10^{-4} M). Line: fitted curve with the optimal fitting parameters $\sigma = 6.4 \times 10^{-3}$, $\gamma = 0.65$, and $\alpha = 1.15$.

by nine polar side chains.[21] They self-assemble into helical aggregates in polar solvents under suitable conditions. Brunsveld et al.[9] synthesized versions of the discotic molecules with chiral and achiral side chains, and performed circular-dichroism measurements on mixtures of these components at the overall concentrations of 10^{-4} and 10^{-5} M in water at 5 °C. They observed a large sergeants-and-soldiers effect, remarkable not only due to the fairly weak bonds between monomers discussed earlier but also because the chiral groups are located in the flexible side chains of the molecules, far from the core which is the main interacting part of the molecule.

In water, Brunsveld et al.[9] observed that the chirality amplification was concentration independent, at least for the two concentrations at which they performed the measurements. As explained in section I, this implies that finite-size effects should not play a role and that our ground-state theory may be used to describe their data. Furthermore, the differences between the chiral and achiral molecules are so small, being a single methyl group on each side chain of the discotic molecules, that we expect that our assumption of equal binding strengths of the chiral and achiral units is justified. It was also observed that the maximum Cotton effect occurs at a fraction chiral material $x < 1$, suggesting that γ must be smaller than unity. This occurrence of a maximum was attributed in ref 9 to a difference in packing between the chiral and achiral molecules due to the presence of the methyl groups in the side chains of the chiral molecules.

In our comparison with the experimental data we fit our theory to the intensity of the Cotton effect at a wavelength of 336−341 nm, divided by the absorption, as a function of the fraction chiral component. We set the maximum in the measured value of this quantity equal to unity, and use the net helicity η' as defined in eq 11 as its theoretical equivalent. The fitting procedure requires the fixing of the cooperativity parameter σ, the parameter α introduced in eq 11, and the ratio of the contributions to the helicity of chiral and achiral monomers γ. One of these we determine independently from the other two. In the small-x regime, the helicity is virtually independent of γ, and we fit this part of the curve with a single parameter, namely σ. To this end, we locate the experimental value for x_*, and fix the value of σ (with $\gamma = \alpha = 1$) at $\sigma = 6.4 \times 10^{-3}$. Using this value, we are able to describe the low-x part of the curve, but not the maximum that occurs in the high-x regime. We fit this part with the two remaining parameters γ and α, and find good agreement between theory and experiment if we set $\alpha = 1.15$ and $\gamma = 0.65$ (see Figure 3).

The value of σ we find corresponds to a helix-reversal energy of $2.5k_BT$, indicating a high degree of cooperativity. This free-energy penalty for a helix reversal is in fact of the same order of magnitude as those found in certain classes of polyisocyanates discussed in the next paragraph. It is also similar to the interfacial penalty between helical and nonhelical regions in aggregates of the chiral C_3 discotic in a different solvent that we found in a previous study.[22] As discussed earlier, we indeed find that a value of $\gamma < 1$ is necessary to describe the maximum found in experiment. This lends support to the suggestion of Brunsveld et al. that packing effects cause this maximum.[9]

For comparison, we also fit our theory to optical-activity measurements of copolymers of (*R*)-2,6-dimethylheptyl isocyanate and *n*-hexyl isocyanate in chloroform at temperatures of −20 and +20 °C,[4,5] although, as mentioned in the Introduction, our theory is strictly not applicable to this type of (conventional polymeric) system. Again we rescale the experimental data (given as the specific rotation vs the mole fraction of chiral monomers) to give unity at the maximum in the curve, and again we determine σ from x_*. We now find $\sigma = 3.1 \times 10^{-4}$ for $T = -20$ °C and $\sigma = 1.2 \times 10^{-3}$ for $T = 20$ °C. Because the maxima in the curves for the isocyanate copolymers occur at relatively high x, quantitative agreement is found already in this regime for a one-parameter fit involving only γ, where α is kept at a value of unity. The curve fit shown in Figure 4 uses the values $\gamma = 0.94$ for $T = -20$ °C and $\gamma = 0.96$ for $T = 20$ °C.

The values of σ we find are in close agreement with values Selinger and Selinger[23] obtained from a fit of both their approximate theory and computer simulation to the same optical-activity measurements on the polyisocyanate system. Apparently, $\sigma = \exp -2R$ is temperature dependent, which is what we expect if the

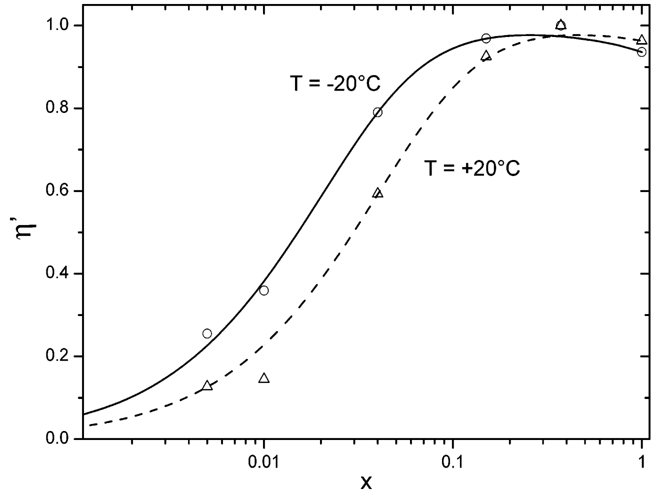

Figure 4. Fit of the theoretical net helicity η' vs x (line) to experimental data of Green et al. at two temperatures. Dashed line (theory) and triangles (experiment): $T = 20$ °C, with fitting parameters $\sigma = 1.2 \times 10^{-3}$ and $\gamma = 0.96$. Solid line (theory) and circles (experiment): $T = -20$ °C, with fitting parameters $\sigma = 3.1 \times 10^{-4}$ and $\gamma = 0.94$.

dimensionless helix reversal free energy R were enthalpy dominated. Is that the case, then from thermodynamics it follows that the ratio of the values of R taken at temperatures T_1 and T_2 obeys $R_2/R_1 \approx T_1/T_2$, which relation is indeed obeyed for the values of R found here.

The reason our theory is able to describe the polyisocyanate experiments is difficult to understand and deserves further study. Naively, one could speculate that the distribution of chiral monomers in the aggregates is similar to that in conventional random copolymers when their fraction is small (i.e., very much smaller than one per bare correlation length). In this case the locations of the chiral monomers within an aggregate are uncorrelated, and truly random. However, this can no longer be the case when the fraction of chiral monomers is not small, and we should therefore expect to see a marked difference between the results for fixed and equilibrium randomness outside of the small-x limit. It may well be that the agreement we observe is merely coincidental. However, we find that our theory is also able to quantitatively fit experimental measurements of the optical activity of a whole range of other copolymers.[3,6,24] In addition to giving experimental results, the authors of ref 24 used the approximate theory of Selinger and Selinger[5] to fit two sets of optical-activity measurements. Our values of R show a reasonable agreement with those obtainable from these fits.

It appears that for the problem studied here, the distinction between an equilibrium type of disorder and a fixed type of disorder is not as large as often thought. From a pragmatic point of view, one may perhaps use our theory even for conventional copolymers, since it gives good agreement with measurements on such polymers, and it is perhaps less cumbersome in its application than existing theories.[2]

IV. Conclusions

The two-component Ising model outlined in this paper provides a quantitative description for the sergeants-and-soldiers principle in self-assembled ("living") polymers, provided they are long enough so that the self-assembly is enslaved by the conformational statistics of the chains. We find that the free-energy penalty associated with a helix reversal is central to the description of the chirality amplification. In this our findings resemble earlier work on conventional ("dead") copolymers.[2,5] Our analytical theory is exact in the infinite-chain limit, and quantitatively describes the Cotton effect as measured by circular dichroism in dilute aqueous solutions of the molecules we refer to as the C_3 discotic, for two concentrations that differ by a factor of 10. We are able to reproduce the experimentally observed maximum in the Cotton effect vs chiral content by following up a suggestion of Brunsveld et al.[9] and assuming a different contribution to the measured helicity of the chiral and achiral monomers. For reasons unclear at this point, our theory also quantitatively describes the sergeants-and-soldiers effect in several conventional copolymers.

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