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COOPERATIVE CHIRAL ORDER IN RANDOM COPOLYMERS

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Abstract A new type of cooperative chiral order has been observed in polyisocyanates composed of a mixture of opposite enantiomers. The chiral order of the copolymer, measured by optical activity, is dominated by whichever enantiomer is in the majority. We present a quantitative theory for this cooperative chiral order, using a mapping of the random copolymer onto the random-field Ising model. Using this theory, we predict how the sharpness of the majority-rule curve can be controlled for applications in a optical switch. We also consider how this theory could be applied to chiral order in DNA.

INTRODUCTION

This paper presents a theory for cooperative chiral order in an unusually simple and well-controlled polymer system. Cooperative chiral order has been the focus of much theoretical and experimental research. Indeed, it has been shown that chirality plays a crucial role in the self-assembly of ordered supramolecular structures in liquid crystals,[1] organic thin films,[2-5] and lipid membranes.[6-12] Those systems are quite complex, and it is difficult to make specific, quantitative comparisons between theoretical predictions and experimental results for them. However, recent experiments by Green *et al.* have discovered a particularly simple and well-controlled example of cooperative chiral order in polyisocyanates formed from a mixture of opposite enantiomers.[13] The chiral order of the copolymer, measured by optical activity, follows a chiral *majority rule*: it is dominated by whichever enantiomer is in the majority.

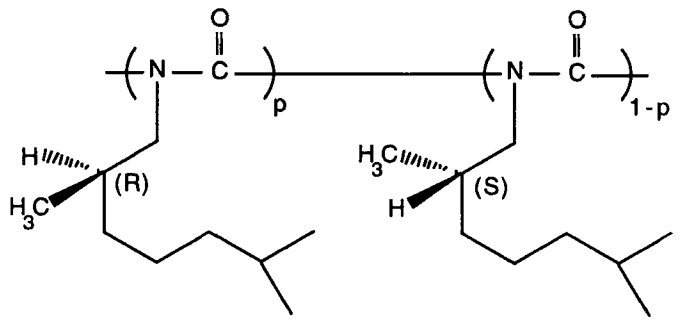

FIGURE 1 Molecular structure of the polyisocyanate with enantiomeric pendant groups derived from citronellic acid, which was studied in Ref. 13.

In this paper, we present a theory for this cooperative chiral order using an analogy with the random-field Ising model, a model that was originally developed to describe random magnetic systems.[14-16] A description of this theory has been published earlier.[17] Using this theory, we predict the chiral order as a function of enantiomer concentration, in quantitative agreement with the experiments. We show that future experiments can control the chiral order by changing two energy scales associated with the chiral packing of monomers. Through changes in these energy scales, the random copolymer can be optimized for use in an optical switch. Finally, we speculate on how this type of theory might be applied to describe chiral order in DNA.

EXPERIMENTAL BACKGROUND

Our theory is based on a series of experiments on polyisocyanates by Green *et al.*[18] Polyisocyanates have the molecular structure shown in Fig. 1. They consist of a carbon-nitrogen backbone with a pendant group attached to each monomer. Several types of pendant groups can be used; in particular, the pendant group can be either chiral or achiral. The backbone itself is achiral. Polyisocyanates are unusual because steric constraints force the molecule into a helical conformation. This helix can be either right-handed or left-

handed. The helical structure of these polymers can be investigated experimentally by measuring their optical activity, i. e., the amount that they rotate the polarization of light. Because the right- and left-handed helices rotate the polarization of light in opposite directions, the optical activity is proportional to the difference in the proportion of right- and left-handed helices.

If the polymers have achiral pendant groups, the right- and left-handed helices have the same energy, and hence are equally likely to occur. For that reason, a solution of such polymers will contain equal numbers of right- and left-handed helices--or if the polymers themselves are long enough, then each chain will contain equal domains of right- and left-handed twist, separated by occasional helix reversals. Hence, the solution will be a racemic mixture, and it will have no net optical activity.

By contrast, if the polymers have chiral pendant groups, the chirality of the pendant groups breaks the symmetry between right- and left-handed helices, and gives an energetic preference for one sense of helicity. This energetic preference leads to net chiral order in the system, and hence to a net optical activity that can be measured experimentally. Even if the pendant groups are only very slightly chiral, they tip the energetic balance between right- and left-handed twist, and give a very substantial optical activity. For example, some experiments have used a deuterated pendant group, which differs from its mirror image only by the substitution of a deuterium for a hydrogen.[19-20] Even that slight difference breaks the symmetry between right- and left-handed polymer helices and induces a large optical activity.

More recently, Green *et al.* have synthesized random copolymers with mixtures of right- and left-handed enantiomeric pendant groups, with concentrations p and $1-p$, respectively.[13] They did not use the deuterated pendant groups; instead they used pendant groups derived from citronellic acid, with a more substantial chirality. Mass-spectrometric analysis of polymer fragments shows that the two types of pendant groups are arranged in a random sequence along the polymer chain.[21] In response to this random sequence of pendant groups, the polymer takes on a conformation with domains of right- and left-handed helicity. A schematic view of this conformation is shown in Fig. 2. The experiments have measured the optical activity as a function of the concentration p. The results, shown in Fig. 3, are quite surprising: For a large range of p, the optical activity is

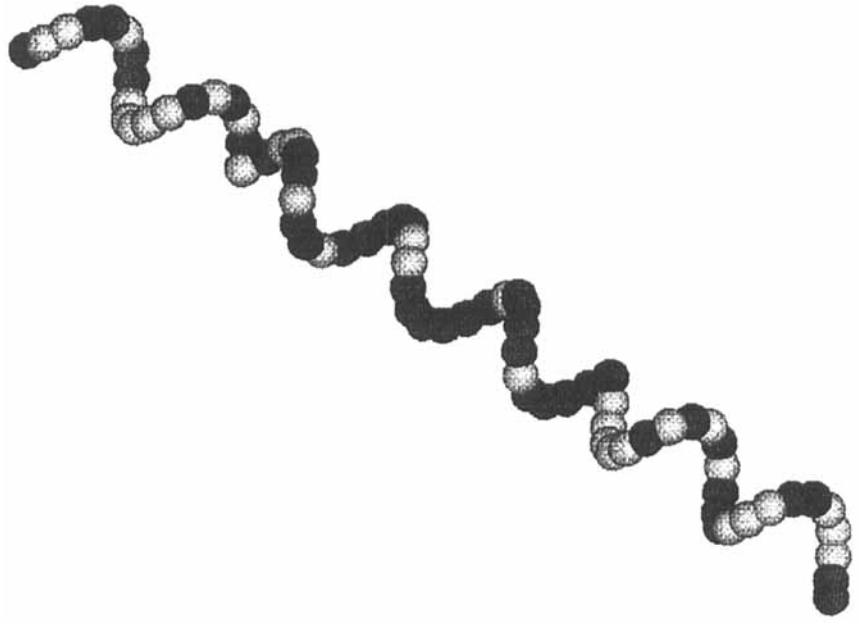

FIGURE 2 Schematic view of the conformation of a random copolymer. The dark spheres represent monomers with right-handed pendant groups, and the light spheres represent monomers with left-handed pendant groups. In response to the sequence of monomers, the polymer takes on a conformation with domains of right- and left-handed helicity. Note that this polymer has two helix reversals.

dominated by whichever enantiomer is in the majority. A 56/44 mixture of enantiomers has almost the same optical activity as a pure 100/0 homopolymer, and even a 51/49 mixture has a third of that optical activity. Green *et al.* have described this phenomenon as *majority rule*. The observation of majority rule shows that chiral order in these copolymers is a highly cooperative effect: Large domains within a copolymer must determine their sense of helicity in response to the random sequence of monomers. In the following section, we present a quantitative theory for this cooperativity.

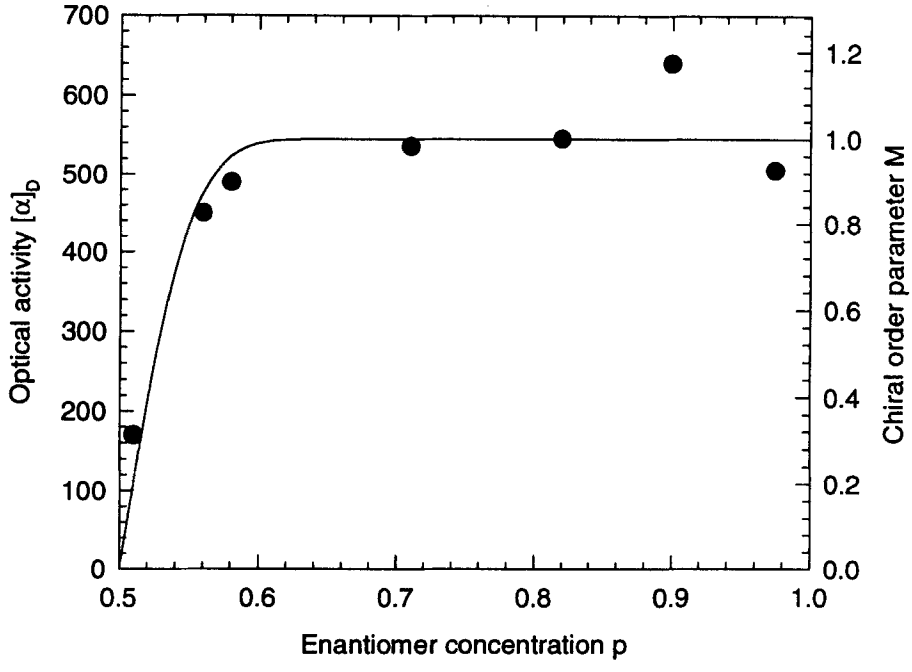

FIGURE 3 Symbols: Optical activity $[\alpha]_D$ of the random copolymer at the sodium D-line as a function of enantiomer concentration p, from Ref. 13. Solid line: Theoretical prediction for the chiral order parameter M from Eq. (5), with the domain size L=164. The prediction agrees with the data with no adjustable parameters, other than the relative scale of the vertical axes.

THEORY

To explain the cooperative chiral order in polyisocyanates, we map these polymers onto the one-dimensional Ising model. First consider homopolymers, with identical pendant groups attached to all the monomers. A homopolymer can be mapped onto the uniform Ising model, with the Hamiltonian

$$H=-J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}-h\sum_{i=1}^{N}\sigma_i, \tag{1}$$

Here, the Ising spin σ_i corresponds to the sense of the polymer helix at monomer i: σ_i=1 represents a right-handed helix and σ_i=-1 a left-handed helix. The number of sites N is the length of the polymer chain. The first term in the Hamiltonian gives the energy cost of a

helix reversal. The second term is the chiral bias, an effective field favoring one sense of the helix, which gives the energy cost of a right-handed pendant group in a left-handed helix (or vice versa). The magnetization of the Ising model,

$$M=\frac{1}{N}\left\langle\sum_{i=1}^{N}\sigma_i\right\rangle, \tag{2}$$

corresponds to the chiral order parameter that is measured by optical activity. Lifson *et al.* earlier derived a similar model for homopolymers, although they used a different notation.[19-20] By fitting the optical activity as a function of temperature, they obtained the helix reversal energy $2J$=17 kJ/mol (4 kcal/mol), and they found that the deuterated pendant groups have a chiral bias $2h$=4 J/mol (1 cal/mol). The chiral bias of the pendant group derived from citronellic acid could not be determined by this fitting, because the optical activity of that homopolymer is saturated for all accessible temperature. However, Lifson *et al.* used molecular modeling to calculate $2h$=1.7 kJ/mol (0.4 kcal/mol) for the pendant group from citronellic acid.[22] These numbers can be compared with the thermal energy k_BT=2.5 kJ/mol (0.6 kcal/mol) at room temperature: The helix reversal energy is large compared to k_BT, while the chiral bias is small (for the pendant group from citronellic acid) or very small (for the deuterated pendant group).

Now consider a random copolymer, with a mixture of right- and left-handed pendant groups. We map the copolymer onto the random-field Ising model,[14-16] which is given by the Hamiltonian

$$H=-J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}-\sum_{i=1}^{N}h_i\sigma_i. \tag{3}$$

Here, h_i corresponds to the enantiomeric identity of the pendant group at monomer i: h_i=+h if it is right-handed (with probability p) and h_i=-h if it is left-handed (with probability 1-p). This field is a *quenched* random variable; it is fixed by the polymerization of each individual chain and does not change in response to changes in the helicity σ_i. Thus, to predict the optical activity of the random copolymer as a function of enantiomer concentration, we must calculate the order parameter M as a function of p, for the given N, J, h, and k_BT.

To calculate the order parameter M approximately, we follow a two-step procedure. First, we note that each chain consists of domains of uniform helicity σ_i. Suppose that each domain has length L, which is to be determined. Each domain responds to the total chiral field $h_{tot}=\sum h_i$ of the monomers in it. Because the domain is uniform, the response is $M(h_{tot})=\tanh(h_{tot}/k_BT)$, equivalent to a single spin in a magnetic field. Averaging over the probability distribution $P(h_{tot})$, we obtain

$$M=\int_{-\infty}^{\infty} dh_{tot} P(h_{tot}) \tanh\left(\frac{h_{tot}}{k_BT}\right). \tag{4}$$

The probability distribution $P(h_{tot})$ is a binomial distribution. For large domains, it can be approximated by a Gaussian with mean $2hL(p-½)$ and standard deviation $2h[Lp(1-p)]^{1/2}$. For $p\approx½$, the standard deviation becomes $hL^{1/2}$. Furthermore, if the width of the Gaussian is much greater than the width of the tanh, $hL^{1/2}\gg k_BT$, then the tanh can be approximated by a step function. These approximations turn out to be self-consistent for the experimental system. The expression for M then becomes

$$M\approx \mathrm{erf}\left[(2L)^{1/2}\left(p-\frac{1}{2}\right)\right]. \tag{5}$$

As a second step, we must estimate the domain size L. The domain size is determined by the density $1/L$ of domain boundaries. Three mechanisms contribute to $1/L$: (a) the density $1/L_{rf}$ of helix reversals induced by the random field, (b) the density $1/L_{th}$ of helix reversals induced by thermal fluctuations, and (c) the density $1/N$ of chain ends. For low densities, these mechanisms should be additive (although they will interact for higher densities). Thus, we expect

$$\frac{1}{L}\approx\frac{1}{L_{rf}}+\frac{1}{L_{th}}+\frac{1}{N}. \tag{6}$$

For $p\approx½$, the random-field domain size can be estimated using a variation of the Imry-Ma argument for the random-field Ising model.[14] A domain forms when the field energy $hL^{1/2}$ grows to equal the boundary energy J. By equating these two energies, we obtain the random-field domain size

$$L_{rf}\approx\left(\frac{J}{h}\right)^2. \tag{7}$$

For the experiments of Green *et al.*, the values $2J$=17 kJ/mol (4 kcal/mol) and $2h$=1.7 kJ/mol (0.4 kcal/mol) are already known. The random-field domain size therefore becomes $L_{rf}\approx 100$ monomers. By comparison, the thermal domain size is $L_{th}=\exp(2J/k_BT)\approx$ 800 monomers, and the chain length is $N\approx$350-5800 monomers. Because L_{rf} is much less than L_{th} and N, we obtain $L\approx L_{rf}$; i. e., the domain size is limited by random-field effects. By plugging this result into Eq. (5), we obtain a prediction for the chiral order parameter M as a function of p.

We must make one remark about these results for the domain size. In general, both L_{rf} and L_{th} depend on p. As p approaches 0 or 1, both L_{rf} and L_{th} should diverge, and each chain should become a single helical domain. The Imry-Ma argument above applies only to the regime where $p\approx$½. This is the appropriate regime for understanding the experiments, because all the significant variation in M occurs around $p\approx$½. Outside that regime, M saturates at ±1, and it is not sensitive to L.

To test this approximate calculation explicitly, we performed numerical simulations of the random-field Ising model. In these simulations, we used a series of chain lengths from 4 to 230, and used the values of J, h, and k_BT from the experiments. For each chain length, we constructed an explicit realization of the random field, then calculated the partition function and order parameter using transfer-matrix techniques. We then averaged the order parameter over at least 1000 realizations of the random field. Figure 4 shows M as a function of p for chain length N=230. These results can be fit very well to Eq. (5), with the domain size $L(230)$=96. The results for other values of N can be fit equally well. Figure 5 shows the fitted domain size $L(N)$ as a function of the chain length N. These results can be extrapolated using $1/L(N)=1/L_{max}+1/N$, to obtain L_{max}=164. This random-field domain size agrees well with Eq. (7), especially considering that the Imry-Ma argument is only a scaling argument. Thus, the chiral order parameter should indeed be given by Eq. (5), with the extrapolated domain size L=164.

To compare our theory with the experiment, we plot our prediction for the chiral order parameter M on top of the experimental data for the optical activity in Fig. 3. The prediction agrees very well with the data. In particular, M saturates at $(p-½)\approx 0.06$, a 56/44 composition, in agreement with the data. This saturation point is a direct measure of $1/(2L)^{1/2}$, which is controlled by the ratio of the two energy scales J and h. We

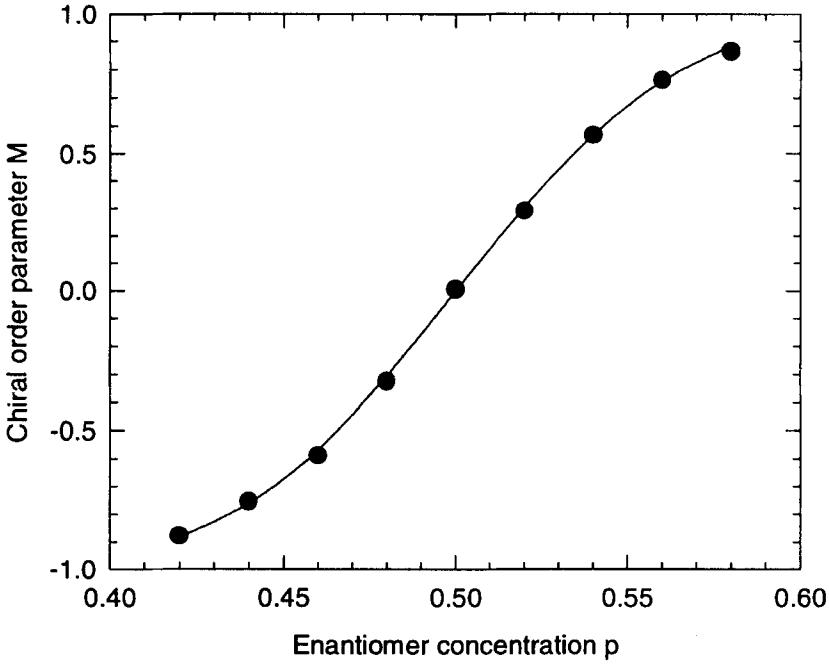

FIGURE 4 Numerical simulation of the chiral order parameter M as a function of enantiomer concentration p for chain length N=230. The solid line shows a fit to the prediction of Eq. (5), which gives the domain size $L(230)$=96.

emphasize that the theory matches the experimental data with *no adjustable parameters*, other than the relative scale of the optical-activity axis and the order-parameter axis. That relative scale is the optical activity of a pure 100/0 homopolymer.

Using our theory, we can make two predictions for future experiments. First, the experiment could be repeated using different chain lengths. For short chains, the domain size L is limited by the chain length N, particularly for $N \lesssim 200$, as shown in Fig. 5. Thus, shorter chains should give a *broader* version of the majority-rule curve. By contrast, longer chains should *not* give a sharper majority-rule curve, because the chains are already in the regime where L is approximately independent of N. Second, the experiment could be repeated using pendant groups that are "less chiral," i. e. polyisocyanates with a lower energy cost for a right-handed monomer in a left-handed helix. A lower value of the chiral field h should give a larger value of the domain size $L \approx (J/h)^2$, and hence a *sharper*

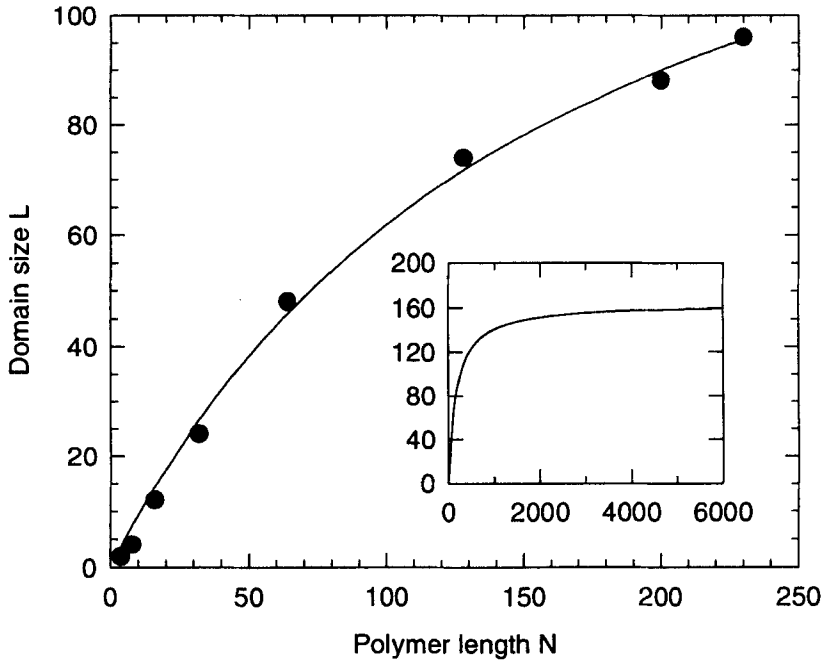

FIGURE 5 The domain size $L(N)$ from numerical simulations for several values of the chain length N. The solid line shows a fit to the extrapolation form $1/L(N)=1/L_{max}+1/N$, or $L(N)=L_{max}N/(L_{max}+N)$, which gives $L_{max}=164$. The inset shows the extrapolation up to $N=6000$.

majority-rule curve. (This prediction applies as long as $L_{rf} \ll L_{th}$, or $2h \gg 2J\exp(-J/k_BT) \approx 0.6$ kJ/mol [0.14 kcal/mol]. Thus, h can be reduced by a factor of 3 from its value in the current experiments, and the majority-rule curve can become 3 times sharper. Beyond that point, the sharpness will be limited by the thermal domain size.) This second prediction might seem counter-intuitive, because one might expect a smaller chiral field to give a smaller effect. However, this prediction is reasonable, considering that the majority-rule curve is limited by the number of monomers that cooperate inside a single domain. If the local chiral field is reduced, then each monomer is more likely to have the same helicity as its neighbors, independent of the local chiral field, and hence the cooperativity increases.

APPLICATIONS FOR ENGINEERING AND FOR BIOLOGY

The unusually sharp dependence of optical activity on enantiomer concentration can be exploited in an optical switch. In one approach to an optical switch currently under development,[23] a mixture of enantiomers is exposed to a pulse of circularly polarized light. Because circularly polarized light is absorbed more by one enantiomer than by the other, the light pulse preferentially excites one enantiomer into a higher-energy state. When that state decays, it can decay into either chiral form. Thus, the light pulse depletes the preferentially excited enantiomer, and changes the enantiomer concentration p. This change in p changes the optical activity of the mixture. Hence, information can be stored in the polymer by writing with a pulse of circularly polarized light, and it can be read with linearly polarized light of the same or different wavelength.

In most chiral materials, this approach is limited by the fact that light pulses only induce a slight change in p, and hence only a slight change in optical activity. However, in the polyisocyanates studied by Green *et al.*, a slight change in p close to $p=½$ is sufficient to induce a very significant change in optical activity. Indeed, this polymer has almost a binary response to changes in p. Thus, this polymer has the characteristic that is needed for an optical switch.

To optimize polyisocyanates for use in an optical switch, one should make the response to changes to p even sharper, i. e. even closer to a binary response. By doing so, one would enhance the change in optical activity that can be achieved by changing p from, for example, 0.49 to 0.51. Our theory predicts which factors control the sharpness of this response and which factors do not. One can make the curve sharper by reducing the chiral bias h or increasing the helix reversal energy J. The chiral bias h can be reduced by synthesizing polymers with new pendant groups, in which the chiral center is farther from the polymer backbone.[24] The helix reversal energy J is harder to change, but it might be increased through other chemical synthesis. By contrast, one *cannot* make the optical-activity curve sharper by reducing the temperature or increasing the chain length, because the system is in a regime where the domain size is not limited by those factors. Thus, our theory indicates how the polyisocyanates can be optimized for use in an optical switch.

Our type of theory might also be applied to describe chiral order in DNA. Like polyisocyanates, DNA consists of a sequence of distinct base pairs, which is fixed by the

polymerization of the molecule. In response to the sequence of base pairs, DNA assumes a helical conformation.[25] For most sequences, the conformation is the right-handed double helix found by Watson and Crick, which is known as B-DNA, with some variations in the conformation that depend on the sequence. However, certain unusual sequences of base pairs give a *left-handed* double helix, known as Z-DNA. The Z-DNA structure was first identified in the sequence CGCGCG; it also occurs in other sequences with alternating pyrimidines and purines.

It may be possible to describe the transition between right-handed B-DNA and left-handed Z-DNA through a model analogous to our model for polyisocyanates. In this model, one would assign an effective chiral field h_i to small groups of bases along the DNA sequence, such as the dinucleotide CG. Most dinucleotides would have a positive value of h_i, representing an energetic preference for a right-handed helix. However, a few dinucleotides, such as CG, would have a negative value of h_i, representing a preference for a left-handed helix. In addition, the parameter J would represent the energy cost of a reversal from B-DNA to Z-DNA along a single DNA molecule. One would then be able to predict the density of Z-DNA domains for a given sequence, based on the statistical frequency of dinucleotides like CG. Such predictions could be tested by measuring the optical activity of DNA that is synthesized with high frequencies of dinucleotides like CG. Of course, this approach to DNA structure is still only speculative, but it indicates how our theory of chiral order in random copolymers could be applied to a biological system.

In conclusion, we have shown that cooperative chiral order in polyisocyanates can be understood through the random-field Ising model. The energy scales J and h, which arise from the chiral packing of the monomers, determine the random-field domain size, which indicates how many monomers are correlated in a single domain. This domain size determines the sharpness of the majority-rule curve. Our theory agrees well with the current experiments, and it shows how future experiments can control the chiral order for technological applications.

ACKNOWLEDGMENTS

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