

Cooperative chiral order in copolymers of chiral and achiral units

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Polyisocyanates can be synthesized with chiral and achiral pendant groups distributed randomly along the chains. The overall chiral order, measured by optical activity, is strongly cooperative and depends sensitively on the concentration of chiral pendant groups. To explain this cooperative chiral order theoretically, we map the random copolymer onto the one-dimensional random-field Ising model. We show that the optical activity as a function of composition is well described by the predictions of this theory. [S1063-651X(97)09602-5]

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In a recent series of experiments, Green *et al.* found that polyisocyanates exhibit a very striking type of cooperative chiral order [1]. Polyisocyanates can be synthesized with any combination of right-handed, left-handed, and achiral pendant groups distributed randomly along the chains. The overall chiral order of the copolymers in solution, as measured by their optical activity, depends sensitively on the concentrations of the different types of pendant groups. Polyisocyanates formed from a mixture of right- and left-handed enantiomers follow a chiral “majority rule” [2]. The optical activity responds sharply to slight differences in the concentrations of the enantiomers, and is dominated by whichever enantiomer is in the majority. Similarly, polyisocyanates with a mixture of right-handed chiral units (known as “sergeants”) and achiral units (known as “soldiers”) are sensitive to very low concentrations of chiral units [3]. They have a substantial optical activity even when the concentration of chiral units is less than 1%. The optical activity of both systems shows a high degree of cooperativity within the copolymers.

In an earlier paper, we proposed a theory for the majority-rule system [4]. The basis of our theory was a mapping of the random copolymer onto the random-field Ising model, a standard model in the theory of random magnetic systems [5,6]. Using this model, we predicted the chiral order of the copolymer as a function of enantiomer concentration, in quantitative agreement with the experiments, and showed that the sharpness of the majority-rule curve is determined by two energy scales associated with the chiral packing of monomers. In this paper, we show that the same type of theory can also explain the chiral order of the sergeants-and-soldiers system. Using the random-field Ising model, we predict the chiral order of these copolymers as a function of the concentration of chiral pendant groups. We show that the measured optical activity is well described by this prediction with a reasonable choice of parameters.

As the material properties of polymers generally depend on a wide variety of chemical and geometric parameters, the present result is remarkable in that it explains the complex behavior of polyisocyanates in terms of a one-dimensional theory with only two material-dependent parameters. That

such a simple theory describes not only one but two different classes of polyisocyanates indicates that the theory accurately represents the physics of cooperative chiral order. Insight from the theory can guide the optimization of material properties for technological applications, as discussed below.

The sergeants-and-soldiers copolymer studied by Green *et al.* is shown in Fig. 1 [3]. This polymer consists of a carbon-nitrogen backbone with a pendant group attached to each monomer. The pendant groups can be either chiral or achiral; the backbone itself is achiral. Steric constraints force the polymer into a helical conformation, which can be either right- or left-handed. The helical structure of the polymers can be investigated experimentally by measuring their optical activity in solution. 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 all the pendant groups are achiral, the right- and left-handed helices have the same energy. A long chain then consists of domains of right- and left-handed helicity, separated by occasional helix reversals. On average, the proportions of right- and left-handed helices are equal, leading to zero net optical activity. However, if a fraction r of the pendant groups are chiral, there is a preference for one sense of helicity, which leads to a net optical activity. Green *et al.* measured the optical activity as a function of r . Their results are plotted in Fig. 2. The measured optical activity is extremely sensitive

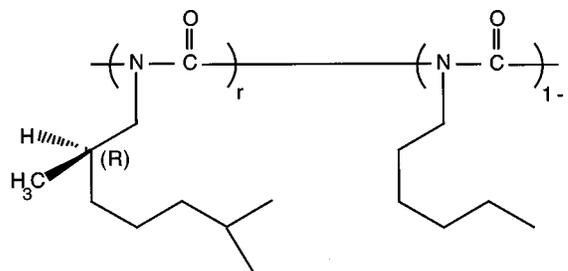


FIG. 1. Molecular structure of the sergeants-and-soldiers copolymer that was studied in Ref. [3]. A fraction r of the pendant groups are chiral (right-handed), and $1-r$ are achiral.

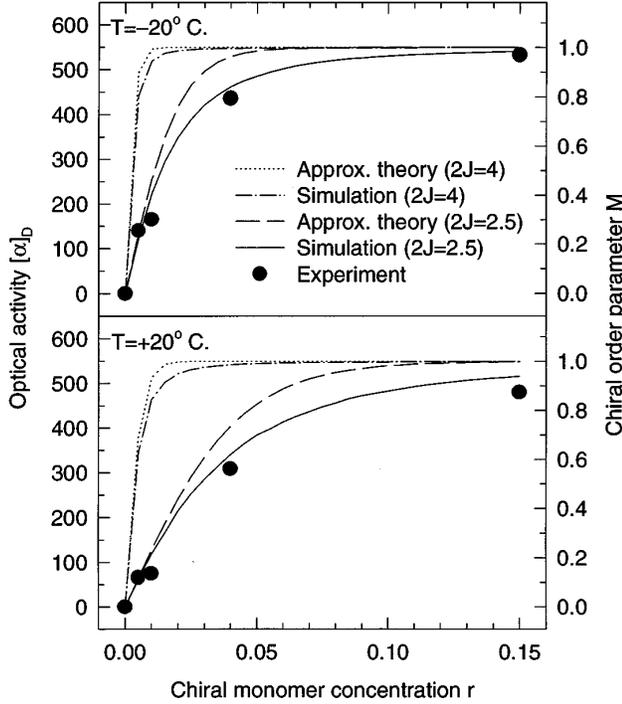


FIG. 2. The symbols show the optical activity $[\alpha]_D$ of the sergeants-and-soldiers copolymer as a function of the chiral monomer concentration r for $T = \pm 20^\circ\text{C}$ from Table I of Ref. [3]. (Data for $r = 0.373$ and $r = 1$ are not shown.) The first pair of lines (dotted and dot-dashed) shows the predictions for the chiral order parameter M from the approximate theory and the simulation with $2h = 0.4$ kcal/mol, $2J = 4$ kcal/mol, and $N = 1000$. The second pair of lines (dashed and solid) shows the predictions for M from the approximate theory and the simulation with $2h = 0.4$ kcal/mol, $2J = 2.5$ kcal/mol, and $N = 1000$. The relative scale of the two vertical axes is the maximum optical activity observed. The second choice of parameters gives good agreement between theory and experiment.

to low concentrations of chiral pendant groups: $r = 0.15$ gives almost the same optical activity as the pure chiral homopolymer with $r = 1$ (not shown in Fig. 2), and even $r = 0.005$ gives a substantial optical activity.

To explain this cooperative chiral order, we map the random copolymer onto the one-dimensional random-field Ising model. In this mapping, the Ising spin σ_i corresponds to the local sense of the polymer helix at monomer i : $\sigma_i = +1$ represents a right-handed helix and $\sigma_i = -1$ a left-handed helix. The Hamiltonian for a copolymer of length N can be written as

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - \sum_{i=1}^N h_i \sigma_i. \quad (1)$$

The first term in this Hamiltonian gives the energy cost of a helix reversal, and the second term gives the local chiral bias, an effective field favoring one sense of the helix. If monomer i is chiral (with probability r) then its chiral bias is $h_i = +h$, and if the monomer is achiral (with probability $1 - r$) then $h_i = 0$. The field h_i is a quenched random vari-

able; it is fixed by the polymerization of each chain and does not change in response to changes in σ_i . The magnetization of the Ising model,

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

corresponds to the chiral order parameter that is measured by the optical activity. To predict the optical activity, we must calculate M .

Before proceeding with the calculation, we note that h and J are approximately known from earlier studies. The parameter $2h$ is the energy cost of a right-handed monomer in a left-handed helix. Through molecular modeling, Lifson *et al.* calculated $2h \approx 0.4$ kcal/mol [7]. The parameter $2J$ is the energy cost of a helix reversal. Through fits of the optical activity of deuterated homopolymers as a function of temperature T , Lifson *et al.* obtained $2J \approx 4$ kcal/mol [8]. The precise value of $2J$ depends on the solvent: it is higher for hexane and lower for chloroform. The majority-rule experiment used hexane [2], while the sergeants-and-soldiers experiment used chloroform [3]. The solvent dependence will be discussed further below. At room temperature, $2J$ is much greater than $k_B T \approx 0.6$ kcal/mol, but $2h < k_B T$. Thus, helix reversals are quite costly in energy, while the chiral bias of a single monomer is fairly small.

To calculate the chiral order parameter M , we follow a procedure analogous to our earlier calculation for the majority-rule system [4]. 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 $h_{\text{tot}} = \sum h_i$ of the monomers in it. Because the domain is uniform, the response is $M(h_{\text{tot}}) = \tanh(h_{\text{tot}}/k_B T)$, equivalent to a single spin in a magnetic field. Averaging over the probability distribution $P(h_{\text{tot}})$, we obtain

$$M = \int_{-\infty}^{\infty} dh_{\text{tot}} P(h_{\text{tot}}) \tanh\left(\frac{h_{\text{tot}}}{k_B T}\right). \quad (3)$$

The probability distribution $P(h_{\text{tot}})$ is a binomial distribution. It can be approximated as follows.

Case A: $rL \ll 1$. In this case, most domains do not have any chiral monomers. We have $h_{\text{tot}} = 0$ with probability $(1 - r)^L$, $h_{\text{tot}} = h$ with probability $Lr(1 - r)^{L-1}$, and $h_{\text{tot}} \geq 2h$ with negligible probability. We can therefore expand Eq. (3) in powers of rL to obtain

$$M \approx rL \tanh \frac{h}{k_B T}. \quad (4)$$

Case B: $rL \gg 1$. In this case, most domains have many chiral monomers. The binomial distribution $P(h_{\text{tot}})$ can then be approximated by a Gaussian with mean hLr and standard deviation $h[Lr(1 - r)]^{1/2}$. Around the peak of the Gaussian, variations in the \tanh in Eq. (3) are negligible. Hence, we obtain

$$M \approx \tanh \frac{rLh}{k_B T}. \quad (5)$$

Note that Eqs. (4) and (5) resulting from cases A and B are quite similar. The limit of Eq. (5) for small rL is $M \approx rLh/k_B T$, which is equivalent to Eq. (4) provided that $h \leq k_B T$. This is valid in the experiments. Hence, it is a good approximation to use Eq. (5) for the whole range of rL .

We must now estimate the characteristic domain size L . The domain size is determined by the density $1/L$ of domain boundaries. Two mechanisms contribute to $1/L$: (a) the density $1/L_{\text{th}}$ of helix reversals induced by thermal fluctuations and (b) the density $1/N$ of chain ends. For low densities, these mechanisms should be additive (although they will interact for higher densities). Hence,

$$\frac{1}{L} \approx \frac{1}{L_{\text{th}}} + \frac{1}{N}. \quad (6)$$

For $r=0$, the thermal domain size is $L_{\text{th}} = e^{2J/k_B T}$. For small nonzero r , we can use this value of L_{th} as an approximation. If $2J=4$ kcal/mol, this size is approximately 2800 monomers at $T=-20$ °C and 960 monomers at $T=+20$ °C. By comparison, the chain length N ranges from 3000 to 10 000 in the experiment [3]. For these values of L_{th} and N , the domain size L is dominated by L_{th} but is somewhat sensitive to N .

We can point out an important difference between the sergeants-and-soldiers system and the majority-rule system considered in our earlier paper [4]. In the majority-rule system, the copolymer has both right-handed monomers with $h_i = +h$ and left-handed monomers with $h_i = -h$. The competition between these fields of opposite signs gives a random-field domain size $L_{\text{rf}} \approx (J/h)^2 \approx 100$. Because L_{rf} is much less than L_{th} and N , the domain size is limited by random-field effects. By contrast, in the sergeants-and-soldiers system, the copolymer has only one type of chiral monomer, so there is no competition between fields of opposite signs. For that reason, the sergeants-and-soldiers copolymer has no random-field domain size; its domain size is limited only by thermal fluctuations and by the chain length. The domain size is therefore much larger in the sergeants-and-soldiers system than in the majority-rule system.

Equations (5) and (6) give a prediction for M as a function of r , h , J , and N . This prediction involves certain approximations—in particular, it neglects the dependence of L on r and h . To test this approximate prediction, we perform numerical simulations of the random-field Ising model. In the simulations, we construct an explicit realization of the random field h_i , then calculate the partition function and order parameter using transfer-matrix techniques. We then average the order parameter over at least 1000 realizations of the random field. In the first series of simulations, we use $2h=0.4$ kcal/mol and $2J=4$ kcal/mol, as in our earlier simulations of the majority-rule system. As discussed above, these parameters are expected to be approximately correct for the sergeants-and-soldiers system. Figure 2 shows the simulation results together with the predictions of the approximate theory for $N=1000$, $T=\pm 20$ °C, and $r=0-0.15$. In most respects, the approximate theory agrees with the simulation. In particular, the approximate theory predicts the slope dM/dr at $r=0$ in agreement with the simulation. (Results for $N=100$, not shown, give equally good agreement between the approximate theory and the

simulation.) There is some discrepancy between the approximate theory and the simulation for larger values of r . This discrepancy arises because the simulation implicitly includes the dependence of L on r and h , so it is more precise than the approximate theory.

Because we have fairly good agreement between the approximate theory and the simulation, we can now compare the theory and simulation with the experimental data in Fig. 2. For this comparison, the relative scale of the optical-activity axis and the order-parameter axis is the maximum optical activity observed. With the parameters $2h=0.4$ kcal/mol and $2J=4$ kcal/mol, the theory and simulation do not agree with the experiment. The prediction for the chiral order parameter saturates much more rapidly than the data for the optical activity. If we used the experimental chain length $N=3000-10\,000$ instead of 1000, the disagreement would be even slightly worse. There may be two reasons why this choice of parameters gave good agreement between theory and experiment in our earlier study of the majority-rule system but poor agreement for the sergeants-and-soldiers system. First, the chiral order of the sergeants-and-soldiers system is dominated by the thermal domain size $L_{\text{th}} = e^{2J/k_B T}$, which is exponentially sensitive to J . Thus, small errors in J have a large effect on the theoretical prediction. By comparison, the chiral order of the majority-rule system is dominated by the random-field domain size $L_{\text{rf}} \approx (J/h)^2$, which is less sensitive to small errors in J . Second, as noted above, the two experiments were done in different solvents: the majority-rule experiment used hexane while the sergeants-and-soldiers experiment used chloroform. Experimental studies of deuterated homopolymers show that the helix reversal energy is lower in chloroform than in hexane [8]. Hence, the disagreement between theory and experiment is probably due to errors in the parameters, particularly J .

To find more accurate values of h and J , we fit the approximate theory to the experimental data using the following procedure. First, we normalize the data for the optical activity by the maximum optical activity observed, to obtain an estimate of M . Next, we determine dM/dr at $r=0$ from the data at each temperature. This gives $dM/dr \approx 54$ at $T=-20$ °C and $dM/dr \approx 26$ at $T=+20$ °C. The approximate theory gives $dM/dr = hL/k_B T = (h/k_B T)e^{2J/k_B T}$ in the limit of large N . Thus, by setting the theoretical prediction for dM/dr equal to the experimental value, we obtain a locus of allowed points in the (h, J) plane for each temperature. Those loci are plotted in Fig. 3. Note that those two curves lie almost on top of each other. They intersect at $2h=0.7$ kcal/mol and $2J=2.2$ kcal/mol, but that intersection is very ill defined numerically. Any point along those curves would give a good fit to the experimental data. For example, $2h=0.4$ kcal/mol and $2J=2.5$ kcal/mol is a reasonable choice, which agrees with the molecular modeling [7] and is roughly consistent with the experiments on deuterated homopolymers [8]. Other points on the curves with lower values of $2h$ and higher values of $2J$ would also be satisfactory.

To test the agreement between theory and experiment for this choice of parameters, we perform a series of simulations with $2h=0.4$ kcal/mol, $2J=2.5$ kcal/mol, $N=1000$, $T=\pm 20$ °C, and $r=0-0.15$. (With these parameters, the thermal domain size is $L_{\text{th}}=144$ at $T=-20$ °C and $L_{\text{th}}=73$ at $T=+20$ °C, which is much less than N , so the

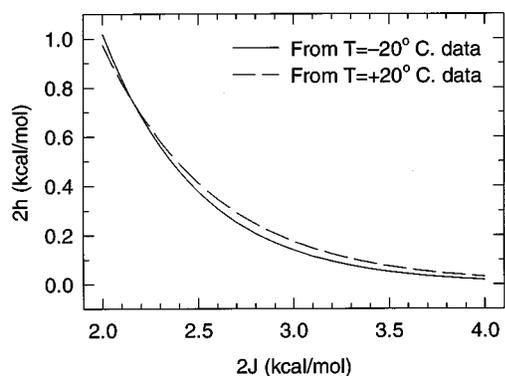


FIG. 3. Loci of values of $2h$ and $2J$ that give good agreement between theory and experiment at $T = \pm 20^\circ\text{C}$.

results are not sensitive to N .) The approximate theory and the simulation results are plotted together with the experimental data in Fig. 2. With these parameters, the approximate theory and the simulation both agree with the experiment. As expected, for larger values of r , the simulation agrees with the experiment even better than the approximate theory does. Thus, the measured optical activity is well described by our theoretical approach with reasonable parameters.

This theory of cooperative chiral order may be useful for technological applications. Zhang and Schuster have proposed a mechanism for an optical switch, which would be controlled by circularly polarized light [9]. The majority-rule system of polyisocyanates would be well suited for this ap-

plication because of the sharp dependence of optical activity on composition near the racemic point. To optimize polyisocyanates for this application, one must know h and J for a variety of pendant groups. So far, h and J have only been measured in experiments on deuterated homopolymers, in which $h \leq k_B T/L$ [8]. If h is larger, the optical activity of a homopolymer is saturated at $M=1$, and no information can be extracted from it. Hence, larger values of h can only be calculated by molecular modeling [7]. Our theory of sergeants-and-soldiers copolymers provides an approach for determining h and J . Future experiments can synthesize sergeants-and-soldiers copolymers with two chain lengths, $N \ll L_{\text{th}}$ and $N \gg L_{\text{th}}$, and several values of r . The parameter h can be determined by fitting the optical activity of the short chains, and the combination $(h/k_B T)e^{2J/k_B T}$ can be determined by fitting the optical activity of the long chains. Through this procedure, experiments can characterize h and J of a variety of polyisocyanates for use in an optical switch.

In conclusion, we have shown that our theoretical approach, based on the random-field Ising model, can explain cooperative chiral order in the sergeants-and-soldiers system as well as the majority-rule system. The sharp increase of the optical activity as a function of chiral monomer concentration depends on the characteristic domain size L , which is determined both by thermal fluctuations and by the chain length. This increase is well described by our theoretical prediction with suitable values of the energy scales h and J .

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