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Cooperative Chiral Order in Polyisocyanates: New Statistical Problems

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ABSTRACT: Polyisocyanates with a random sequence of (*R*) and (*S*) pendant groups follow a chiral "majority rule": the optical activity of the polymers is dominated by whichever enantiomer is in the majority. In earlier work, this effect was explained theoretically through a mapping of the polymer system onto the random-field Ising model. Here, the theory is extended to a wider class of heteropolymers. The theory predicts that the introduction of achiral pendant groups into the random sequence should have remarkably little effect on the sharpness of the majority-rule curve. It further predicts that correlations in the handedness of neighboring pendant groups should reduce the sharpness of the majority-rule effect, while anticorrelations should enhance the sharpness of this effect.

Introduction

Polyisocyanates are a class of polymers exhibiting a remarkable type of cooperative chiral order.[1] Polyisocyanates can be synthesized with any combination of (*R*), (*S*), and achiral pendant groups distributed randomly along the chains. In response to the sequence of pendant groups, the polymer adopts a conformation with segments of right- and left-handed helicity. The relative proportions of right- and left-handed segments can be determined by measuring the optical activity of the polymers in dilute solution. In a series of experiments, Green et al. found that the optical activity of polyisocyanates is extremely sensitive to slight chiral influences.[1] For example, in polyisocyanates with a random sequence of (*R*) and (*S*) pendant groups, the optical activity responds sharply to a slight excess of (*R*) over (*S*) units.[2] This behavior was therefore called a chiral "majority rule." Likewise, in polyisocyanates with a random sequence of (*R*) pendant groups and achiral pendant groups, the optical activity responds sharply to slight concentrations of chiral units.[3] The chiral units were therefore called "sergeants" and the achiral units "soldiers." Both the majority-rule effect and the sergeants-and-soldiers effect are signs of a high degree of cooperativity along the polymer chains.

In earlier papers, we presented a theory of cooperative chiral order in polyisocyanates.[4,5] This theory was based on a mapping of the polymers onto the random-field Ising model, a standard model in the theory of random magnetic systems.[7,8] Using this theory, we calculated the chiral order of the polymers as a function of composition in the majority-rule system[4] and the sergeants-and-soldiers system.[5] In both cases, the theoretical results were in quantitative agreement with the experiments. Related theoretical work has been done by Gu et al.[6] In this paper, we apply our theoretical approach to two new statistical problems concerning cooperative chiral order in polyisocyanates. First, we consider the diluted majority-rule effect in terpolymers with random sequences of (*R*), (*S*), and achiral pendant groups. One might expect that the dilution of chiral pendant groups by achiral pendant groups would make the majority-rule curve much broader. However, our calculation shows that the introduction of achiral pendant groups has surprisingly little effect on the sharpness of the majority-rule effect. The enantiomeric excess that is required to saturate the optical activity is approximately independent of the concentration of achiral pendant groups, up to very high concentrations. These predictions are consistent with preliminary unpublished experiments, and further experimental tests are in progress.[9] Second, we consider polymers with correlations or anticorrelations in the handedness of neighboring pendant groups. Our calculation shows that correlations between neighboring pendant groups make the majority-rule effect broader, while anticorrelations make the majority-rule effect sharper. These predictions can be tested in future experiments.

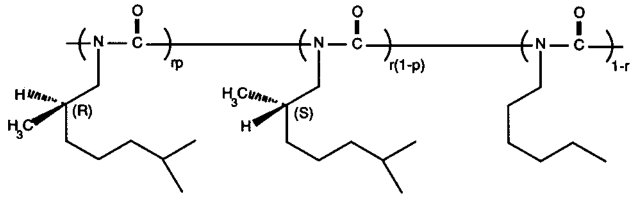

Figure 1. Molecular structure of the polyisocyanates studied experimentally in refs 2 and 3. In this paper, we consider terpolymers with a fraction *rp* of (*R*) pendant groups, *r*(1 − *p*) of (*S*) pendant groups, and 1 − *r* of achiral pendant groups.

Diluted Majority Rule

The molecular structure of polyisocyanates is shown in Figure 1. The polymer has a carbon−nitrogen backbone with a pendant group attached to each monomer. In general, the polymer can have a statistical distribution of (*R*), (*S*), and achiral pendant groups. The fraction of each species along the chain is fixed at the time the polymer is formed, according to its density in the prepared solution. Present sample preparation methods appear to introduce no correlations in pendant species along the chain.[10] Because of packing constraints, the backbone is forced into a helical conformation, which can be right- or left-handed. (*R*) and (*S*)

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pendant groups favor opposite senses of the polymer helix, while achiral pendant groups are neutral. As a result, the polymer has local segments of right- and left-handed helicity. The relative proportions of right- and left-handed helical segments can be determined experimentally by measuring the optical activity of a dilute solution of polyisocyanates in an organic solvent.

In earlier work, we described this polymer system theoretically by mapping it onto the random-field Ising model.[4,5] In this mapping, the local sense of the polymer helix at monomer i is represented by the Ising spin σ_i, with $\sigma_i = +1$ corresponding to a right-handed helix and $\sigma_i = -1$ to a left-handed helix. The Hamiltonian for a polymer of length N can then be written as

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

The first term in the Hamiltonian gives the energy cost of a helix reversal, while the second term gives the local chiral bias, an effective field due to the pendant group at site i, which favors one sense of the helix. An (R) pendant group has $h_i = +h$, an (S) pendant group has $h_i = -h$, and an achiral pendant group has $h_i = 0$. The field h_i is a quenched random variable, which is fixed by the polymerization of each chain and does not change in response to changes in σ_i. The chiral order parameter measured by the optical activity is then proportional to the magnetization of the Ising model,

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

Hence, the goal of the theory is to calculate M for any statistical distribution of the (R), (S), and achiral pendant groups, as a function of their relative concentrations, the temperature T, and the chain length N.

Our earlier papers considered two specific statistical distributions of pendant groups: the majority-rule system, with a random sequence of (R) and (S) units,[4] and the sergeants-and-soldiers system, with a random sequence of (R) and achiral units.[5] In both cases, our theoretical results for the chiral order parameter M were consistent with experimental measurements of the optical activity by Green et al.[2,3] Here, we consider the more general case of a polymer with a random sequence of (R), (S), and achiral pendant groups. There are two reasons for investigating this terpolymer system. First, the optical activity of terpolymers can be measured in an extension of earlier work.[9] We would like to make predictions for terpolymers that can be tested in these experiments. Second, the majority-rule system of polyisocyanates is well suited for applications in optical switching[11] because of the sharp dependence of optical activity on composition near the racemic point. To reduce the cost of the polymers for applications, one might want to substitute less expensive achiral pendant groups in place of some fraction of the more expensive chiral pendant groups. This substitution would also allow variation in the material characteristics and response speed of the polymers. We would like to determine how this change will affect the performance of an optical switch.

In the terpolymer, let r be the fraction of all pendant groups that are chiral, and let p be the fraction of chiral pendant groups that are (R). Hence, the chain has a fraction rp of (R) pendant groups, $r(1 - p)$ of (S) pendant groups, and $1 - r$ of achiral pendant groups, as shown in Figure 1. To calculate the chiral order parameter for this system, we follow a procedure analogous to our earlier calculation for the majority-rule system.[4] We note that each chain consists of domains of uniform helicity σ_i, and we 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 $P(h_{\text{tot}})$ gives

$$M = \int_{-\infty}^{\infty} \mathrm{d}h_{\text{tot}}\, P(h_{\text{tot}}) \tanh\left(\frac{h_{\text{tot}}}{k_{\text{B}} T}\right) \tag{3}$$

The probability distribution $P(h_{\text{tot}})$ is a trinomial distribution, the natural generalization of the binomial distribution considered in ref 4. For large domains, it can be approximated by a Gaussian with mean $2hLr(p - {}^1/_2)$ and standard deviation $h\{Lr[1 - r + 4rp(1 - p)]\}^{1/2}$. For $p \approx {}^1/_2$, the standard deviation becomes $h(Lr)^{1/2}$. Furthermore, if the width of the Gaussian is much greater than the width of the tanh, $h(Lr)^{1/2} \gg k_{\text{B}}T$, then the tanh can be approximated by a step function. The expression for M then becomes

$$M \approx \operatorname{erf}\left[(2Lr)^{1/2}\left(p - \frac{1}{2}\right)\right] \tag{4}$$

Hence, at an enantiomeric excess of $(p - {}^1/_2) \approx (2Lr)^{-1/2}$, M grows to $\operatorname{erf}(1) \approx 0.84$; i.e., the optical activity is 84% of its maximum possible value. We will refer to this level as the saturation point.

The second half of the calculation is to estimate the domain size L. The characteristic domain size is determined by the density $1/L$ of helix reversals. Three mechanisms contribute to $1/L$: (a) the density $1/L_{\text{rf}}$ of helix reversals induced by the random field, (b) the density $1/L_{\text{th}}$ of helix reversals induced by thermal fluctuations, and (c) the density $1/N$ of chain ends. For low densities (i.e., large L), these mechanisms should be additive, although they will interact for higher densities. Hence,

$$\frac{1}{L} \approx \frac{1}{L_{\text{rf}}} + \frac{1}{L_{\text{th}}} + \frac{1}{N} \tag{5}$$

For $p \approx {}^1/_2$, the random-field domain size L_{rf} can be estimated using a variation of the Imry–Ma scaling argument for the random-field Ising model.[7] A domain forms when the field energy $h(Lr)^{1/2}$ grows to equal the boundary energy J. By equating these two energies, we obtain the random-field domain size

$$L_{\text{rf}} \approx \frac{1}{r}\left(\frac{J}{h}\right)^2 \tag{6}$$

By comparison, the thermal domain size is $L_{\text{th}} = e^{2J/k_{\text{B}}T}$, and the chain length N is the degree of polymerization of the chains. Hence, eqs 4–6 give an approximate prediction for the chiral order parameter of the terpolymer.

In the majority-rule system studied experimentally,[2,4] the random-field domain size L_{rf} is much less than the thermal domain size L_{th} and the chain length N. Hence, that system has $L \approx L_{\text{rf}}$; i.e., the domain size is limited by random-field effects. Suppose we now introduce a small fraction $1 - r$ of achiral pendant groups into that system. Equation 6 shows that L_{rf} increases as r decreases. However, for a small fraction of achiral pendant groups, L_{rf} will still be much smaller than L_{th} and N, so the system will still have $L \approx L_{\mathrm{rf}}$. We can therefore insert our expression 6 for L_{rf} into eq 4 for the chiral order parameter M. This calculation shows that the factors of r exactly cancel out of the prediction for M. The chiral order parameter saturates at an enantiomeric excess of

$$\left(p - \frac{1}{2}\right) \approx \frac{h}{2^{1/2}J} \tag{7}$$

independent of r. Thus, a small fraction of achiral pendant groups should have *no effect* on the sharpness of the majority-rule curve for M as a function of p. As the achiral fraction $1 - r$ increases, there will be no effect until L_{rf} grows comparable to L_{th} or N, so that thermal effects or chain length limit the sharpness of the majority-rule curve. This crossover occurs at

$$r \approx \left(\frac{J}{h}\right)^2 \left(\frac{1}{L_{\mathrm{th}}} + \frac{1}{N}\right) \tag{8}$$

A further decrease in the chiral fraction r (i.e., increase in the achiral fraction $1 - r$) beyond that point will make the majority-rule curve broader.

Note that the crossover value of r given by eq 8 can be quite small. For the majority-rule system studied experimentally, the parameters $2J \approx 4$ kcal/mol and $2h \approx 0.4$ kcal/mol are known.[2,4,12,13] At room temperature, we have $k_{\mathrm{B}}T = 0.6$ kcal/mol, so the thermal domain size is $L_{\mathrm{th}} \approx 800$ monomers. The crossover value of r depends on the chain length N. For chains of length $N = 200$ monomers, that crossover value is $r \approx 0.6$. In other words, the sharpness of the majority-rule curve should be approximately independent of the fraction of achiral pendant groups up to an achiral fraction of 40%, which is surprisingly high. For chains of length $N = 20\,000$ monomers, the crossover value becomes $r \approx 0.13$. In that case, the sharpness of the majority-rule curve should be approximately independent of the achiral fraction up to 87% achiral, which is even more remarkable. This result is contrary to the expectation that the introduction of any achiral pendant groups should make the majority-rule curve much broader. However, the result is reasonable because the sharpness of the majority-rule curve depends on the number of independent chiral units within a single cooperative domain. The introduction of achiral pendant groups leaves the number of cooperating chiral units unchanged, as long as the random-field domain size L_{rf} is much less than the thermal domain size L_{th} and the chain length N.

To test these approximate theoretical predictions, we performed a series of numerical simulations of the random-field Ising model for the terpolymer. In these simulations we constructed an explicit realization of the random field h_i and 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. We used the known parameters $2J = 4$ kcal/mol and $2h = 0.4$ kcal/mol, simulated room temperature $k_{\mathrm{B}}T = 0.6$ kcal/mol, and used the chain length $N = 200$ monomers. This chain length is shorter than the typical experimental value, but it is convenient for the simulations. The numerical results are presented in Figure 2. This figure shows the majority-rule curve for M as a function of p for three values of r: $r = 1.0$ (no achiral pendant groups), $r = 0.6$ (40% achiral pendant groups), and $r = 0.2$ (80% achiral pendant groups). We can see that the introduction of 40% achiral pendant groups makes the curve only slightly broader, while the introduction of 80% achiral pendant groups makes the curve substantially broader. The solid lines in the figure show the predictions of our approximate theory.[14] These predictions are consistent with the simulation results, and they describe the dependence of M on r as well as p. Preliminary experiments have confirmed that the sharpness of the majority-rule curve is independent of r over a wide range of r.[9] In these experiments, N is much greater than 200 monomers and $2J$ is believed to be greater than 4 kcal/mol, so the sharpness is independent of r over an even wider range than in the simulations. More detailed experimental tests of our predictions are in progress.

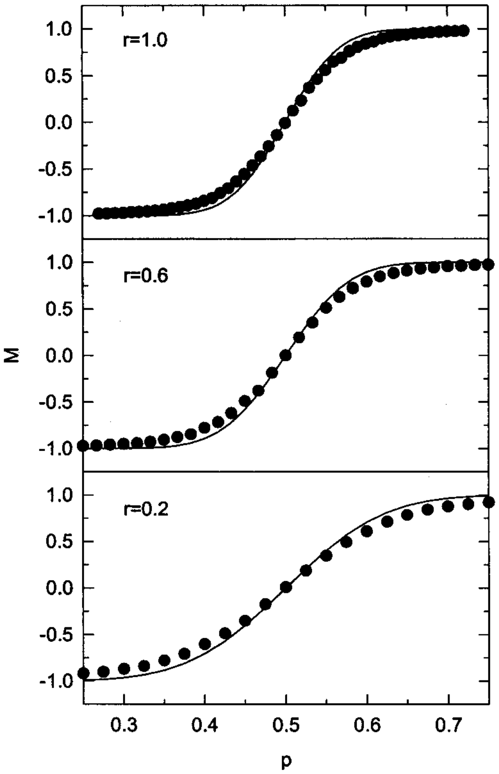

Figure 2. Chiral order in terpolymers of length $N = 200$ monomers. The chiral order parameter M is plotted as a function of p, the fraction of chiral pendant groups that are (R), for three values of r, the fraction of all pendant groups that are chiral. The symbols represent the simulation results, and the solid lines represent the approximate theoretical prediction of eq 4.

Correlations and Anticorrelations between Neighboring Pendant Groups

We now consider a second new statistical problem in the theory of polyisocyanates. So far, we have assumed that there are no correlations in the handedness of neighboring pendant groups along a polymer chain. This assumption is justified for the majority-rule system by experiments that deuterated the (S) monomers, synthesized the polymers, broke the polymers into trimers, and then analyzed the trimers using mass spectrometry.[10] However, future experiments might synthesize

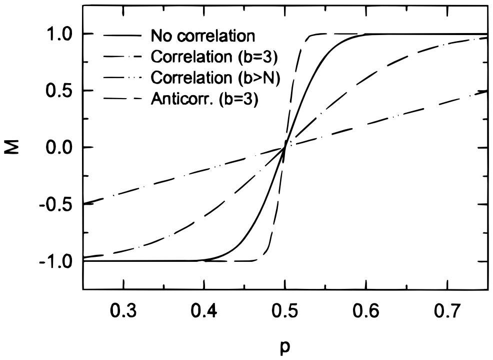

Figure 3. Effects of correlations and anticorrelations in the handedness of neighboring pendant groups on the majority-rule curve in polyisocyanates. The chiral order parameter M is plotted as a function of the (R) monomer concentration p for polymers with no correlations, correlations with block size $b = 3$, long-range correlations with b greater than the chain length N, and anticorrelations with $b = 3$.

polymers with correlations in the handedness of neighboring pendant groups, so that an (R) pendant group is more likely to be followed by another (R) than by an (S). This could be done, for example, by synthesizing oligomers of pure (R) or pure (S) monomers and then linking the oligomers into block copolymers. Alternatively, experiments might synthesize polymers with anticorrelations in the handedness of neighboring pendant groups, so that an (R) pendant group is more likely to be followed by an (S) than by another (R). For that reason, we would like to predict how correlations and anticorrelations in the handedness of neighboring pendant groups affect the sharpness of the majority-rule curve.

In this calculation, we consider polymers composed of only (R) and (S) pendant groups, without any achiral pendant groups. We concentrate on the effects of the correlated random field and neglect the effects of thermal fluctuations and chain length.

As a simple model of correlations between neighboring pendant groups, we suppose that a polymer consists of blocks with b identical pendant groups: $(RR\cdots R)$ or $(SS\cdots S)$. To determine the effect of the correlations, we regard the blocks rather than the monomers as the fundamental units of the polymer. In this renormalized description of the polymer, a fraction p' of the blocks are all (R), and they have a chiral field of $+h'$. The remaining $1 - p'$ of the blocks are all (S), with a chiral field of $-h'$. The block variables p' and h' are related to the monomer variables p and h by

$$\left(p' - \frac{1}{2}\right) \approx \left(p - \frac{1}{2}\right) \qquad h' = bh \tag{9}$$

The helix reversal energy $2J$ is the same in the block description as in the monomer description. By applying eq 7 to the block description, we see that the chiral order parameter saturates at $(p' - {}^1/_2) \approx h'/(2^{1/2}J)$. Translating that equation into the monomer description, we find that saturation occurs at

$$\left(p - \frac{1}{2}\right) \approx \frac{bh}{2^{1/2}J} \tag{10}$$

Hence, the correlation between neighboring pendant groups makes the majority-rule curve *broader* by a factor of b, as shown in Figure 3. One must go to a larger enantiomeric excess to saturate the optical activity than in the case of no correlations. This broadening is reasonable in the limit of large b. For $b > N$, each chain is composed entirely of (R) or (S) pendant groups. The chiral order parameter M is then proportional to the difference in concentrations of (R) and (S) chains, which is just a straight line in Figure 3.

To model anticorrelations between neighboring pendant groups, we suppose that a polymer consists of blocks with b alternating pendant groups: $(RSRS\cdots R)$ or $(SRSR\cdots S)$. We assume that b is odd, so that each block has a net excess of one (R) or one (S). Again, we regard the blocks rather than the monomers as the fundamental units of the polymer. A fraction p' of the blocks are mostly (R), with a chiral field of $+h'$, and the remaining $1 - p'$ of the blocks are mostly (S), with a chiral field of $-h'$. In this anticorrelated system, the block variables p' and h' are related to the monomer variables p and h by

$$\left(p' - \frac{1}{2}\right) = b\left(p - \frac{1}{2}\right) \qquad h' = h \tag{11}$$

Applying eq 7 to the block description shows that the chiral order parameter saturates at $(p' - {}^1/_2) \approx h'/(2^{1/2}J)$. Hence, in the monomer description, the saturation occurs at

$$\left(p - \frac{1}{2}\right) \approx \frac{h}{2^{1/2}bJ} \tag{12}$$

The anticorrelation between neighboring pendant groups therefore makes the majority-rule curve *sharper* by a factor of b, as shown in Figure 3. This result is important because it shows that the sharpness of the majority-rule effect can be enhanced by changing the statistical distribution of the pendant groups, without synthesizing new pendant groups.

The effect of block size on the majority-rule curve can be understood intuitively by an analogy with voting. In elections, voters are generally divided into districts, each of which chooses one representative. If the districts are composed of large correlated blocks of majority-party voters or minority-party voters, then the representation of the minority-party voters is enhanced, compared with a random distribution of voters among districts. This proportional representation corresponds to a broader majority-rule effect in polyisocyanates. Conversely, if the districts are composed of anticorrelated groups of majority-party and minority-party voters together, then the representation of minority-party voters is suppressed, compared with a random distribution of voters. That scenario corresponds to a sharper majority-rule effect in polyisocyanates.

In conclusion, we have extended our theory of cooperative chiral order to a wider class of random heteropolymers. The theory predicts that the introduction of achiral pendant groups does not affect the majority-rule curve, until one reaches very high concentrations of achiral pendant groups. The theory also predicts that correlations in the handedness of neighboring pendant groups make the majority-rule curve broader, while anticorrelations make the curve sharper. These predictions can all be tested by experiments on polyisocyanates.

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(14) Details of the derivation of the theoretical curves: Our earlier simulations of the majority-rule system (with $r = 1$) showed that $(L_{\mathrm{rf}}^{-1} + L_{\mathrm{th}}^{-1})^{-1} \approx 164$. Because $L_{\mathrm{th}} = e^{2J/k_{\mathrm{B}}T} = 786$, this result implies that $L_{\mathrm{rf}} \approx 207$. This is consistent with the scaling estimate of eq 6, considering the uncertainty that is inherent in a scaling estimate. Hence, for the theoretical curves in Figure 2, we used $L_{\mathrm{rf}} = 207/r$, $L_{\mathrm{th}} = 786$, and $N = 200$ in eqs 4 and 5.

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