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Switching a Helical Polymer between Mirror Images Using Circularly Polarized Light

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Abstract: A system has been created in which chiral information inherent in circularly polarized light can be used to influence the helical sense characteristics of a polymer. A racemic mixture of a photoresolvable ketone-containing group was appended through different linkage patterns to a polymer having dynamically interconverting equal populations of left- and right-handed helical backbone conformations. Irradiation with circularly polarized light in the ketone's chromophore gave rise to easily measurable circular dichroism signals in the polymer backbone helix, which changed sign with a change in the sense of the circularly polarized light. This demonstrates that the small enantiomeric excess produced by the irradiation, even diluted with large proportions of achiral pendants, is capable of enforcing a disproportionate excess of one helical sense in the polymer. The results, expressed as optical activity as a function of the degree of polymerization, could be analyzed using an approximate solution of a one-dimensional quenched random-field Ising model. The experimental data were fit to the theory and demonstrated a crossover between statistical and thermal randomness in the response of the helical sense to the chiral information generated by the light.

Introduction

Photoresolution is the process whereby one enantiomer of a racemic mixture is enriched by its preferential absorption of one-handedness of circularly polarized light (CPL).[1,2] There is great interest in understanding and exploiting this phenomenon, since it has been proposed as a possible source of life's homochirality,[3] and because it has been identified as having potential utility in the development of light-driven devices.[4−11]

Photoresolution processes may be either reversible or irreversible. Both cases begin with a racemic mixture of enantiomers that is stable and noninterconverting in the absence of light. For irreversible reactions, excitation of either enantiomer of the starting material (S_S or S_R) causes conversion to a product, which is a different substance that may not be chiral. The relative concentrations of S_S and S_R change as this reaction proceeds under the influence of CPL because (+)CPL is absorbed by S_S with a different probability (expressed as the extinction coefficient, ϵ) than is (−)CPL. This differential absorption is referred to as circular dichroism, and the magnitude of this effect is expressed as the difference in extinction coefficients ($\Delta\epsilon$) between S_S and S_R with (+) or (−)CPL. The enantiomeric excess (ee) ultimately achieved in an irreversible photoresolution depends on $\Delta\epsilon$ and the extent of reaction. At very high conversion, the small amount of remaining starting material can have a very high ee.[12,13]

Reversible photoresolution is the opposite of photoracemization, $S_S \rightarrow (S_R + S_S)$, which results when irradiation of one enantiomer causes its conversion to an equal mixture of both enantiomers. In this case, because of circular dichroism, irradiation of a racemic mixture of S_S and S_R with CPL gives an optically active, partially resolved mixture. In contrast to the irreversible process, the ee achieved in the reversible photoresolution reaches a constant value at a photostationary state (γ_{PSS}), which is determined by the Kuhn anisotropy factor[14−16] ($g_\lambda = \Delta\epsilon/\epsilon$) according to: $\gamma_{PSS} = {}^1/_2 g_\lambda$. The partially resolved mixture ($[S_S] > [S_R]$) can be easily returned to the racemic form ($[S_S] = [S_R]$) by irradiation with unpolarized light, or converted to the opposite optically active mixture ($[S_S] < [S_R]$) by irradiation with the other-handedness of CPL. Unfortunately, the magnitudes of g_λ, and the corresponding values for γ_{PSS}, that can be achieved are usually very small; for typical

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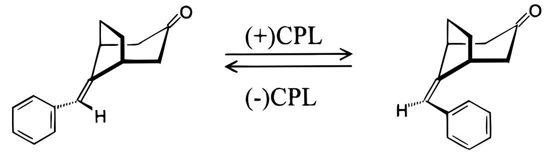
organic chromophores, g_λ is ~10^{-4}.[17−19] There has been a search for compounds having atypically large values of g_λ that will undergo reversible photoresolution,[10,11] and for the physical means to amplify the small ee that can be achieved by this route.

Schuster and co-workers discovered that the styryl-substituted, axially chiral bicyclo[3.2.1]octan-3-one derivative (**1**) has the properties required for reversible photoresolution.[20] It is stable in the absence of light, but irradiation of resolved **1** leads to its efficient photoracemization with no detectable decomposition. Racemization of **1** results from rotation around the stryryl double bond in the triplet state of this group. The styryl excited state is formed by intramolecular triplet−triplet energy transfer from the ketone group, which absorbs the light. The Kuhn anisotropy of chiral ketones can be large because their nπ* transitions are electronic symmetry forbidden.[21−23] This is particularly true of compounds with a rigid framework, which inhibits averaging of conformations having oppositely signed circular dichroism (CD) spectra.[24] Calculation from the CD and absorption spectra of **1** reveal a maximum value for the Kuhn anisotropy factor in the nπ* absorption at 313 nm where $g_{313} = 0.05$; a value about 500 times greater than that of most organic compounds. This is confirmed by irradiation of racemic **1** with CPL, which leads to its reversible photoresolution yielding $ee_{PSS} = 1.5\%$, a value greater than that reported for any other stable organic compound. In the work reported here, we investigate a physical means to amplify the nonracemic properties of photoresolved **1**.



(R)-**1** (S)-**1**

The unique properties of liquid crystals provide one means for amplification and translation of the small enantiomeric excess produced by a reversible photoresolution. Schuster and Burnham recently reported the light-driven, reversible conversion of nematic and cholesteric materials by alternating photoresolution and photoracemization of a trigger with structure closely related to **1**.[25]

A second means for physical amplification of small enantiomeric excesses comes from recent discoveries about the structural properties of polyisocyanates.[26−31] These stiff polymers exist as equally populated dynamically interconverting right- and left-handed helices separated by infrequent helical reversals whose relative populations are extraordinarily sensitive to chiral perturbation.[30,32−34] Remarkably, the random incorporation of a few chiral pendant groups with ee close to the racemic state converts the polymer to one having an out-of-proportion excess of one helical sense. The minority enantiomeric group takes on the helical sense of the majority enantiomer to avoid intervention of energetic helical reversals. Green and co-workers have characterized this phenomenon as "majority rules",[29] since the net helical sense of the polyisocyanate is controlled by the chiral pendant group with the greatest representation. The chiral amplification that results from the majority rule in polyisocyanates is large. For example, a terpolyisocyanate formed from inclusion of 1.6% of a chiral group having an ee of only 2.8% shows a strong preference for one helical sense.[35] The magnitude of the majority rule chiral amplification in polyisocyanates has been analyzed by Green and Selinger and successfully fit to a one-dimensional Ising model.[30,36,37]

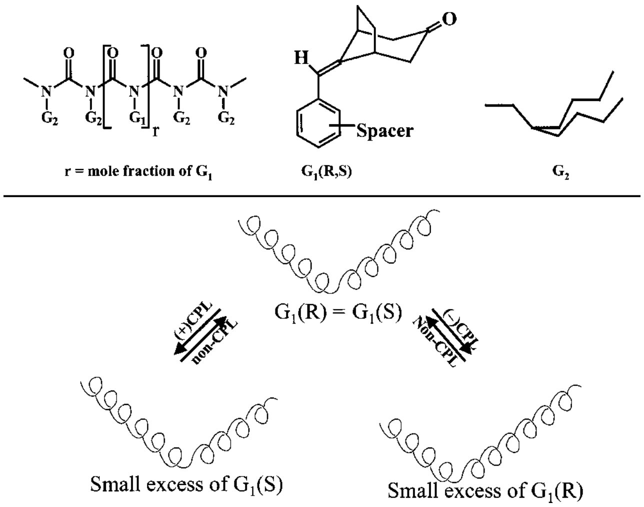


Figure 1. Schematic representation of the shift between right- and left-handed backbone helices of a polyisocyanate with bicycloketone chromophore pendants subjected to irradiation with (+) or (−) circularly polarized light (CPL) or noncircularly polarized light (non-CPL); the excess helical sense shown for the (+) or (−)CPL corresponds to experiments with polymers in series III; the excess of one helical sense over the other is schematic.

Clearly, the exceptional sensitivity of polyisocyanates provides a possible physical means for amplification of the optical activity formed by photoresolution of a chiral pendant group. The majority rule or "diluted majority rule" effect[38] seems ideally suited to transfer chiral information encoded in CPL and amplify it with the chiral response of a polymer. This concept is outlined in Figure 1 in which alternating photoresolution and photoracemization of a chiral pendant group, G_1, converts a polymer from an equal population of left- and right-handed helices to one containing a majority helical sense. Herein we report the development of chiral pendant groups related to **1** and their incorporation in polyisocyanates. Irradiation of these polymers with CPL results in their reversible interconversion between racemic and optically active forms that is sensed by

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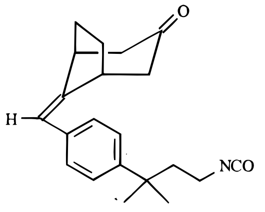
Chart 1



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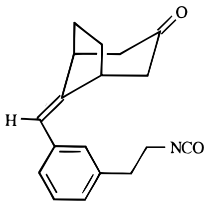

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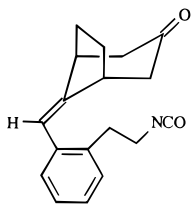

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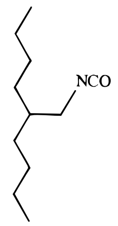

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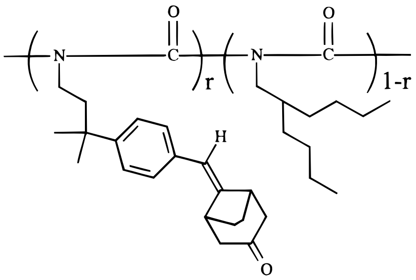
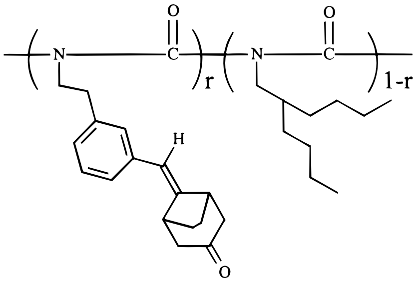
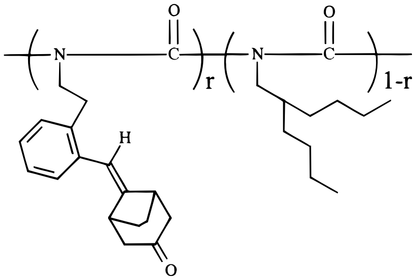
Chart 2



para-terpolymer series: *para*-**I**



meta-copolymer (r = 1)
meta-terpolymer series: *meta*-**II**



ortho-copolymer (r = 1)
ortho-terpolymer series: *ortho*-**III**

changes in their circular dichroism spectra. A statistical analysis of the connection between the chiral properties of the side chains and the helical sense properties of the polymer backbone shows excellent agreement with the predictions of a quenched random field one-dimensional Ising model.

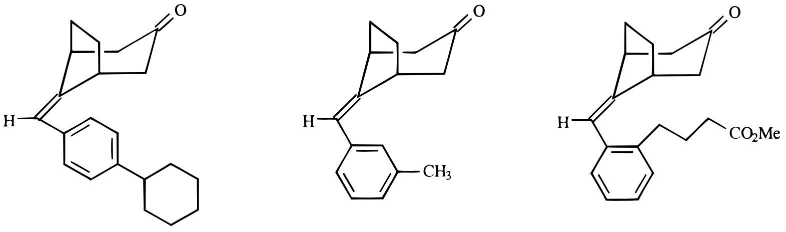
Results

Selection of a photoresolvable functional group and adapting it so that it can be incorporated in a polyisocyanate are the first steps required in the investigation of the creation of helical polymers that can be switched between mirror images with CPL. For the reasons elucidated above, we focused our effort on styryl-substituted bicyclo[3.2.1]octan-3-ones. In principle, this structure can be incorporated into a polymer by linking an isocyanate group either to the bicyclic skeleton or to the styryl portion of the molecule. We chose the latter option because it provides an opportunity for systematic structural variation. Variants of the bicyclic ketone with two or three-atom linkers connecting the *para*, *meta*, and *ortho* positions to an isocyanate group (Chart 1: **2**, **3**, and **4**) were prepared and investigated. The synthesis and characterization of these monomers will be reported elsewhere.

The three bicyclic ketone monomers of Chart 1 were used to prepare three polymer series (**I**, **II**, **III**) by their reaction in DMF solution initiated with NaCN. The colorless polymers were purified further by reprecipitation, which gives fiberlike materials. Each series may contain two classes of polymers: a copolymer formed from a racemic mixture of the bicyclic ketone monomers, or a terpolymer formed by reaction of the bicyclic ketone monomers with an achiral alkyl comonomer. Each class of terpolymers contains a range of materials having different ratios of bicyclic ketone monomer and the achiral alkyl comonomer. The polymers prepared in this work are shown schematically in Chart 2, where *r* represents the mole fraction of bicyclic ketone monomer. We selected 2-*n*-butylhexyl isocyanate (**5**, see Chart 1) as the achiral alkyl comonomer because it forms soluble polymers and because its branched alkyl group gives the polymer a high helical reversal energy (ΔG_r), a parameter closely connected to the chiral amplification.[35] Preliminary experiments with polymers in the *para*-substituted series **I** showed only a very small response of the chiral properties of the polymer to the photoresolution of its chiral pendant group, presumably because of the separation between the chiral information and the polymer backbone (see below). Consequently, the *para* system was not studied in detail.

Characterization of the Polymers. Each of the polymers prepared was analyzed by ^{1}H NMR and UV spectroscopy. In each case, the NMR spectrum showed that the ratio of monomers in the polymer is essentially the same as their ratio in the polymerized monomer mixture. GPC analysis of the copolymers prepared from racemic monomer **3** or **4** shows polydisperse materials of relatively low molecular weight (MW).

Chart 3



6 **7** **8**

Table 1. Characterization of the Polymer Series **I**, **II**, and **III** by GPC

polymer entry	r/mol %	M_w/1000	M_n/1000	polydispersity index
para-**I**	0.22	70	35	2.0
para-**I**	0.06	226	81	2.8
meta-**II**	1	27	11	2.4
meta-**II**	0.09	256	75	3.4
meta-**II**	0.05	420	102	4.1
meta-**II**	0.02	623	424	1.5
ortho-**III**	1	16	5	3.1
ortho-**III**	0.16	63	23	2.8
ortho-**III**	0.1	104	36	2.9
ortho-**III**	0.4	319	84	3.0
ortho-**III**	0.02	405	108	3.8

The MW of the terpolymers formed from reaction of alkyl achiral comonomer **5** and racemic monomers **2**, **3**, or **4** depends on the mole fraction, r. The smaller the r, the higher is the MW. These data are summarized in Table 1. The copolymers are soluble in THF and CH_2Cl_2; the terpolymers are also soluble in *n*-hexane solution.

Chiroptical Properties of the Bicyclic Ketone Derivatives. The chiroptical properties of organic compounds are sensitive to perturbation by electronic or steric interaction with substituents. For this reason, the chiroptical properties of the ketone-containing pendant groups on polyisocyanates **I**, **II**, and **III** are expected to differ from those of **1**. We examined the effect of the linker group on the spectral and photochemical properties of the styryl-substituted bicyclic ketones. Since the isocyanates are air- and moisture-sensitive, analogues were used in these experiments. Model compounds **6**, **7** and **8** (Chart 3) were selected because they can be resolved into enantiomers chromatographically and because their spectral properties were expected to be similar to those of **2**, **3** and **4**, respectively.

The enantiomers of bicyclic ketone analogues **6**, **7,** and **8** were partially resolved by HPLC with a chiral stationary phase. Their UV and CD spectra, shown in Figures 2 and 3, respectively, are essentially identical with those of the chromophore of the pendant groups they are designed to mimic. Thus, they are suitable models for the ketone chromophores of polyisocyanates **I**, **II,** and **III**. Calculation of g_λ from these data shows that γ_{313} is 1.7% for **6**, 1.2% for **7**, and 0.97% for **8**.

CPL ($\lambda > 305$ nm) was generated by passing the light from a Hg(Xe) lamp sequentially through a cutoff filter, a Glan-Taylor linear polarizer, and then a Fresnel rhomb. The handedness of the CPL was selected as (+) or (−) by a 90° rotation of the linear polarizer. The irradiation of racemic **6**, **7,** or **8** with CPL results in partial photoresolution with ee_{pss} (determined from the CD spectra of the irradiated solutions) of 1.3, 1.0, and 0.65%, respectively. These findings are in accord with those predicted from the spectroscopic results, and they permit the quantitative analysis of the photoresolution of polymers **II** and **III**.

Photoresolution of Polymers I, II, and III. Incorporation of the styryl-substituted bicyclic ketone group in a polyisocyanate could affect its photochemical behavior. For example, its intramolecular reaction with other pendant groups might cause its consumption, or the polyamide backbone might compete with the styryl group for the triplet energy of the ketone. In fact, irradiation of N_2-saturated, room-temperature solutions of polymers **I**, **II**, or **III** with CPL ($\lambda > 305$ nm) results in no measurable (by UV spectroscopy) consumption of the ketone group: however, CD spectroscopy shows that their bicyclic ketone groups are photoresolved. The polyamide backbone does not absorb in the ketone nπ^* region at 300 nm. The UV spectra of the polymers are the sum of the absorption of the polyamide backbone ($\lambda_{max} = 255$ nm) and the styryl-substituted ketone comonomer $\pi\pi^*$ transition ($\lambda_{max} \approx 250$) and its weaker n$\pi^*$ transition ($\lambda_{max} \approx 300$ nm). However, irradiation of each polymer with CPL generates a CD spectrum that mirrors the nπ^* absorption of the ketone, Figure 4. As a control, we showed that changing (+)CPL to (−) reverses the sign of this CD signal. These results confirm the successful photoresolution of the pendant ketone groups of the polymers.

The influence of the photoresolved pendant ketone groups on the polyisocyanate helix direction was also probed by CD spectroscopy. Polyisocyanates with optically active, but nonabsorbing pendant groups, have CD spectra with maxima at ~255 nm, which corresponds to the absorption of the polyamide backbone.[30] The CD spectrum of photoresolved polymer **I** ($r = 6\%$) shows no signal in this region. Evidently, partial resolution of the *para*-linked ketone group on this polymer does not shift the population of M and P backbone helices. In contrast, irradiation of *meta*-polymers **II** or *ortho*-polymers **III** does result in generation of CD signals at 255 nm, Figure 5. In these cases, the optical activity transferred from the CPL to the ketone group controls the backbone helical sense of the polymer. Interestingly, the CD sign at 255 nm of *meta*-terpolymer **II** is opposite that of *ortho*-terpolymer **III**, although both polymers were irradiated with (+)CPL. The sign change indicates that the same enantiomer of resolved pendant ketone linked in a different manner can induce opposite helical twists of the polymer backbone. The interaction energy between the ketone groups and the polymer is expected to be very small, and the interactions responsible for the sign reversal may therefore be impossible to identify with current theoretical tools.[39]

A primary objective of this work was to demonstrate that the helical sense of a polyisocyanate could be reversibly switched with CPL. Figure 6 shows that irradiation of *meta*-terpolymer **II** ($r = 2\%$) with (+)CPL causes photoresolution of the pendant ketone group and enforces the majority rule on the polyisocyanate helix, which is revealed by its CD spectrum. Further irradiation of this solution with unpolarized light racemizes the ketone and causes the polymer to return to a state having equal proportions of right- and left-handed helices. Finally, irradiation of *meta*-terpolymer **II** with (−)CPL reinstates

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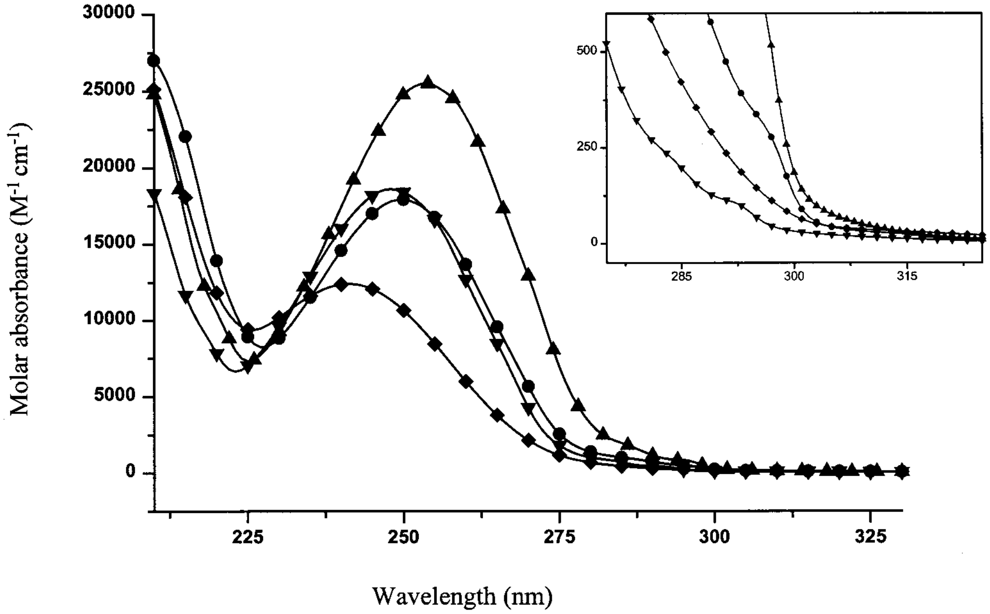

Figure 2. UV absorption spectra of **1** (- -▼- -), model compounds **6** (- -▲- -), **7** (- -●- -), and **8** (- -◆- -) in cyclohexane solution.

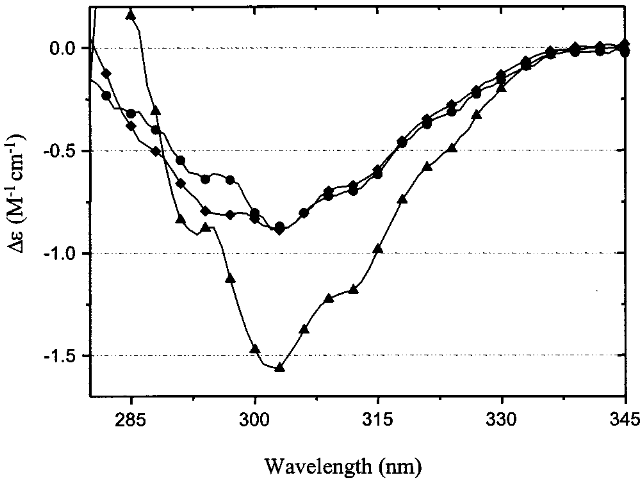

Figure 3. The wavelength dependence of $\Delta\epsilon$ for model compounds **6** (- -▲- -), **7** (- -●- -), and **8** (- -◆- -) in cyclohexane solution measured at the ketone $n\pi^*$ absorption region (~ 300 nm).

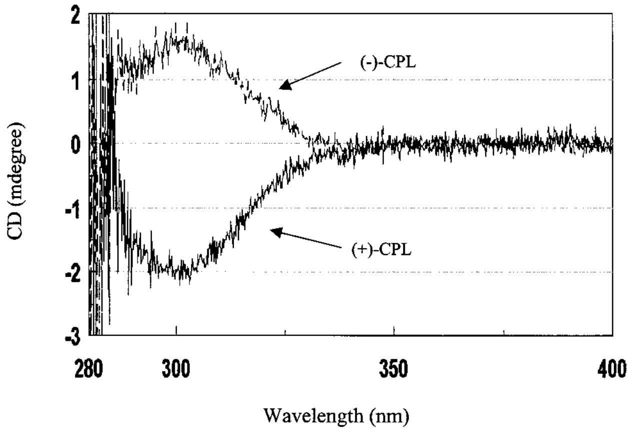

Figure 4. CD spectra of *para*-terpolymer **I** ($r = 6\%$) irradiated in ketone $n\pi^*$ absorption region (~300 nm) with CPL, recorded in *n*-hexane solution (4 mg/mL, 0.5 cm path length).

the majority rule, but the opposite excess helical sense is enforced. Similar results, also shown in Figure 6, are obtained with the *ortho*-copolymer **III** and with *ortho*-terpolymer **III** ($r = 4\%$). This is the first example we are aware of in which the chirality of light is captured by a chemical reaction and then amplified by controlling the conformation of a polymer backbone.

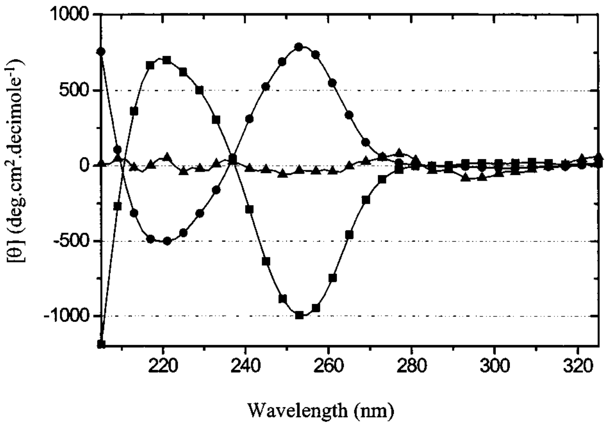

Figure 5. The wavelength dependence of $[\theta]$ for of *para*-terpolymer **I** ($r = 6\%$) - -▲- -, *meta*-terpolymer **II** ($r = 2\%$) - -●- -, and *ortho*-terpolymer **III** ($r = 2\%$) - -■- -. irradiated with (+)CPL in *n*-hexane solution.

Effect of Polymer Composition and Chain Length on Chiral Amplification. Polymer composition is a fundamental variable that might affect the magnitude and sign of the majority rule response. We examined the effect of varying the mole fraction of bicyclic ketone pendant group, *r*, from 2 to 100%. Interestingly, the results are different in the *meta*-polymer **II** than they are in the *ortho*-polymer **III** series. Figure 7 shows the CD spectra, plotted as molar ellipticity, $[\theta]$, for polymers in series **II** that had been irradiated with (+)CPL to their photostationary state. The copolymer ($r = 100\%$) has the greatest ellipticity, and the magnitude of $[\theta]$ decreases as *r* decreases, but all series **II** polymers have CD spectra with the same sign. Figure 8 shows the results of similar experiments with polymers in series **III**. In contrast to series **II**, the sign of the CD spectrum changes between the copolymer and the terpolymer, and changing *r* in the terpolymer between 2% and 16% has little effect on $[\theta]$. The interaction between the excess enantiomer of the pendant group produced by irradiation with

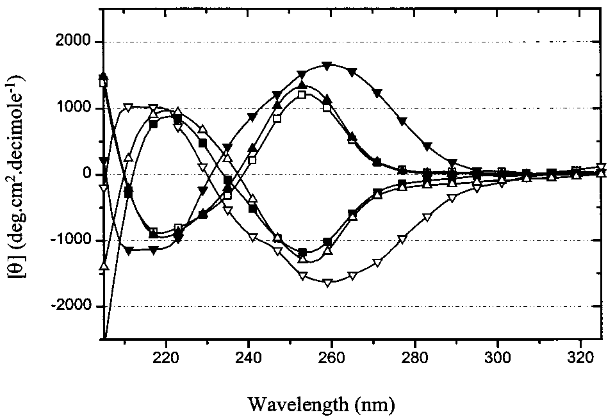

Figure 6. The wavelength dependence of [θ] (molar ellipticity) for *ortho*-copolymer in methylene chloride and THF (1: 1) solution (- -▼▽- -), *meta*-terpolymers **II** (r = 2%) in *n*-hexane solution (- -▲△- -), and *ortho*-terpolymer **III** (r = 4%) in *n*-hexane solution (- -■□- -) irradiated with CPL. The filled uptriangle, down-triangle and square are CD spectra of the polymers irradiated with (+)-CPL and the open uptriangle, down-triangle and square are CD spectra of the polymers irradiated with (−)CPL.

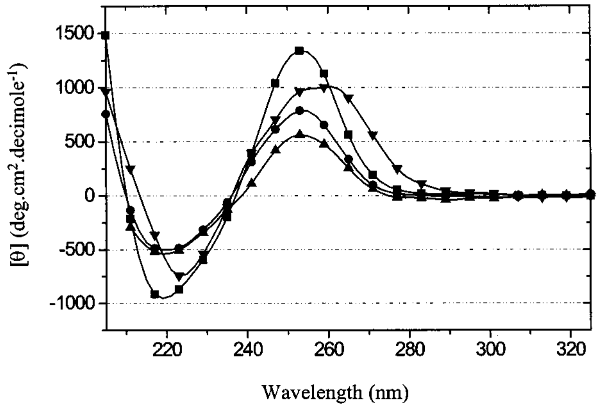

Figure 7. The wavelength dependence of [θ] (molar ellipticity) for the *meta*-copolymer **II** (r = 100%, - -▼- -) measured in THF solution, *meta*-terpolymer **II** (r = 9%, - -▲- -), *meta*-terpolymer **II** (r = 5%, - -●- -) and *meta*-terpolymer **II** (r = 2%, - -■- -) measured in *n*-hexane solution after irradiation with (+)CPL.

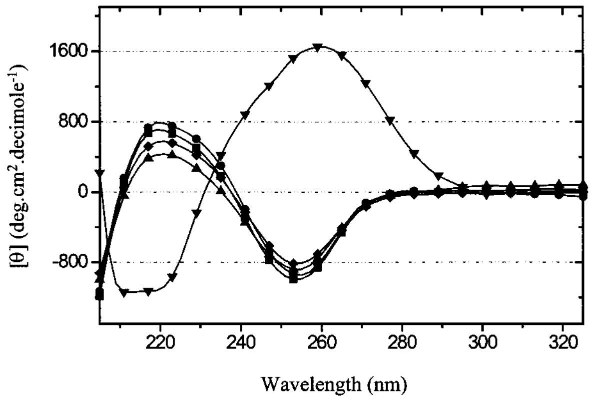

Figure 8. The wavelength dependence of [θ] (molar ellipticity) for *ortho*-copolymer **III** (r = 100%, - -▼- -) measured in THF and methylene chloride (1:1) solution, *ortho*-terpolymer **III** (r = 16%, - -▲- -) measured in THF and *n*-hexane (1:3) solution, *ortho*-terpolymer **III** (r = 10%, - -●- -), *ortho*-terpolymer **III** (r = 4%, - -■- -), and *ortho*-terpolymer **III** (r = 2%, - -◆- -) measured in *n*-hexane solution after irradiation with (+)CPL.

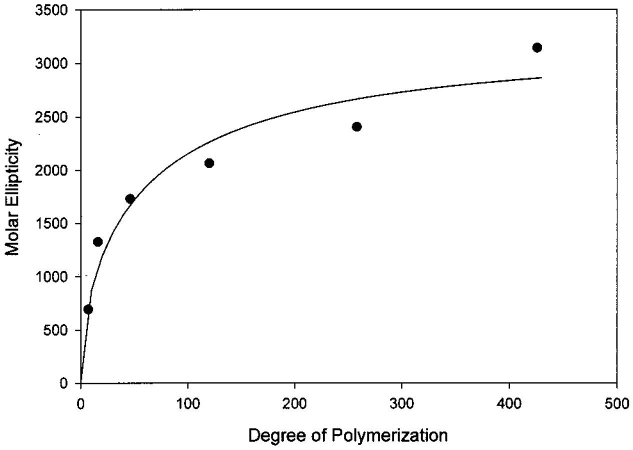

Figure 9. Molar ellipticity [θ], measured at 254 nm, of GPC fractionated samples of the *ortho*-copolymers plotted as a function of degree of polymerization. The points are the experimental measurements; the line is the theoretical fit to the one-dimensional quenched random-field Ising model.

CPL to the excess helical sense of the backbone is difficult to assign to a specific structural source since the chiral bias energies may be quite small and therefore difficult to interpret as has been discussed above.[39] Such small chiral biases may change sign in surprising ways, as has been seen before.[40,41]

These findings confirm that chiral amplification is provided by the polymer: a small percentage of chiral pendant groups (2%) with an ee of less than 1% dispersed randomly among a large excess of achiral pendants (98%) are sufficient to give an easily measured optical activity. The sense of the excess helix can be assigned tentatively based on the correlation of the sign of the CD spectrum to a standard optically active polymer, which has been the subject of a force field calculation.[42] In the case of **III** (r = 2%) this excess sense is left-handed for irradiation with (+)CPL.

The one-dimensional quenched random-field Ising model (see below) predicts that [θ] will respond differently to the polymer MW depending on the magnitude of the interaction energy (ΔG_h) between the chiral pendant and the helix. This prediction was probed by fractionation, by gel permeation chromatography, of photoresolved copolymers and terpolymers in the *meta* and *ortho* series. The magnitude of [θ] for the chromophore of the helical polyamide backbone was determined for each fraction by measurement of its CD spectrum. Figures 9−12 show the results obtained for *meta*-terpolymer **II** (r = 2%), *ortho*-terpolymer **III** (r = 2%), and their corresponding copolymers (r = 100%). The correlation of the experimental results with the predictions from the theory is remarkably good. The one-dimensional quenched random-field Ising model not only predicts the functional form of the MW dependence of [θ], but it also provides, as discussed in detail below, a reliable measure of the ee_{PSS} of the pedant ketone groups.

Discussion

Optical organic molecular switches, in which information is recorded and erased reversibly by light, have potential value in data storage, in micro-structuring of interfaces, in the design of photoresponsive chromatographic matrices, and the development

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[40] Green, M. M.; Khatri, C. A.; Peterson, N. C. *J. Am. Chem. Soc.* **1993**, *115*, 4941.

[41] Khatri, C. A.; Pavlova, Y.; Green, M. M.; Morawetz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6991.

[42] Lifson, S. F.; Felder, C. E.; Green, M. M. *Macromolecules* **1992**, *25*, 4142.

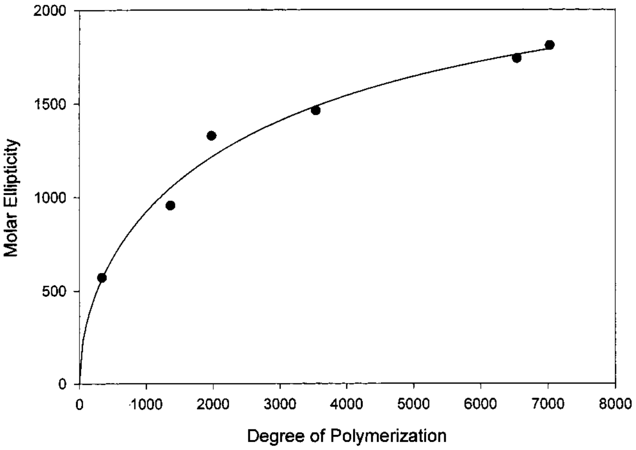

Figure 10. Molar ellipticity [θ], measured at 254 nm, of GPC fractionated samples of the *ortho*-terpolymer **III** ($r = 2\%$) plotted as a function of degree of polymerization. The points are the experimental measurements; the line is the theoretical fit to the one-dimensional quenched random-field Ising model.

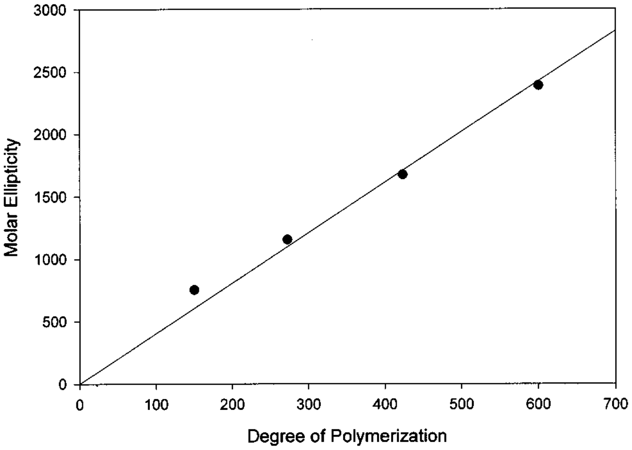

Figure 11. Molar ellipticity [θ], measured at 254 nm, of GPC fractionated samples of the *meta*-copolymer plotted as a function of degree of polymerization. The points are the experimental measurements; the line is the theoretical fit to the one-dimensional quenched random-field Ising model.

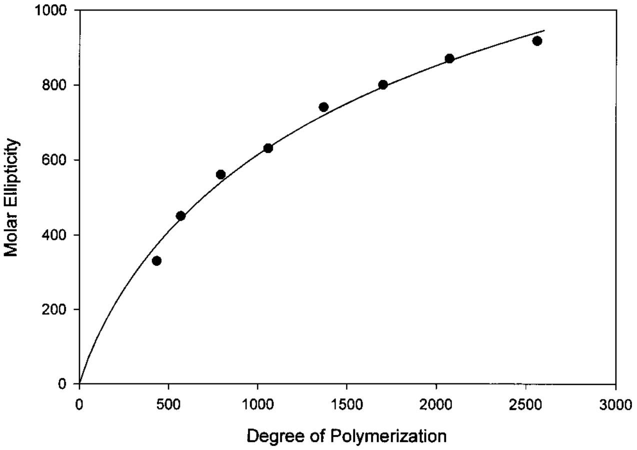

Figure 12. Molar ellipticity (θ), measured at 254 nm, of GPC fractionated samples of the *meta*-terpolymer **II** ($r = 2\%$) plotted as a function of degree of polymerization. The points are the experimental measurements; the line is the theoretical fit to the one-dimensional quenched random-field Ising model.

of target-activated therapeutic agents.[43] A suitable optical switch requires two thermally stable states that can be distinguished and switched reversibly by light. The findings described above demonstrate experimentally for the first time the reversible control of a polymer backbone's helicity with CPL. By incorporating a bicycloketone chromophore into a polyisocyanate backbone, a system has been created in which chiral information inherent in circularly polarized light can be used to control the helically derived optical properties of the polymer. The bicycloketone group controls the dynamically interconverting populations of left- and right-handed helical polyisocyanate backbone conformations. Irradiation of the bicycloketone group with CPL results in easily measurable circular dichroism signals attributed to the helical conformation of the amide backbone of the polyisocyanate. This optical signal is persistent until it is erased by irradiation with unpolarized light. These findings demonstrate that the minute enantiomeric excess produced by irradiation with CPL is capable of being transferred to the polyisocyanate backbone, leading to an excess of one helical sense of the polymer chain becoming predominant over the other. The results, expressed as the optical activity as a function of the degree of polymerization, are analyzed using an approximate solution of a one-dimensional quenched random field Ising model, which is described below. The systems reported here are, however, not suitable for development as devices because the rate of approach to the photostationary state, which depends exponentially on g_λ, is too slow. Nevertheless, these results are a clear demonstration of the principles required for the control and amplification of reactions sensitive to the sense of CPL, and they provide insight into opportunities to develop additional systems tailored so that the response to light produces a desirable physical outcome.

The Quenched Random-Field Ising Model. The extent of chirality transfer from the bicyclic ketone group to the polymer backbone is determined by the free-energy difference ΔG_h between the diastereomers (M-helix + *R*-pendant) and (P-helix + *R*-pendant).[36-38,44-46] This diastereomeric free-energy difference can be expected to be highly dependent upon the distance between the chiral pendants and polymer backbone. With a large distance between the bicyclic ketone group and the polymer backbone (i.e., polymer series **I** case), the bicyclic ketone will have little interaction with the polymer backbone so that the interconversion of the bicyclic ketone enantiomers will lead to no free-energy difference between the M- and P-helices. This, as we have seen for *para*-terpolymer **I** in Figure 5, is observed. In contrast, *meta*- and *ortho*-linked bicyclic ketones, with shorter distance to the polymer backbone, can interact efficiently. However, the *meta*-linked case induces an opposite helical sense preference in the polymer amide chain than the *ortho*-linked group. This must be related to the detailed interaction by which the chiral pendants approach the polymer backbone, of which little is known.

The experimental results can be explained by a theory of chiral order in random heteropolymers.[36-38,44-46] This theory uses the quenched random-field Ising model to describe polymers composed of a random sequence of (*R*), (*S*), and achiral monomers. Let r be the fraction of monomers that are chiral, and p be the fraction of chiral monomers that are (*R*).

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(43) Wilner, I.; Wilner, B. *Adv. Mater.* **1995**, *7*, 587.

(44) Okamoto, Y.; Matsuda, M.; Nakano, T.; Yashima, E. *Polym. J.* **1993**, *25*, 391.

(45) Okamoto, Y.; Mukaida, F.; Gu, H.; Nakamura, Y.; Sato, T.; Teramoto, A.; Green, M. M.; Andreola, C.; Peterson, N. C.; Lifson, S. *Macromolecules* **1996**, *29*, 2878.

(46) Gu, H.; Sato, T.; Teramoto, A.; Varichon, L.; Green, M. M. *Polym. J.* **1997**, *29*, 77.

The theory then predicts the excess helical sense M, the fraction of the chain that is a right-handed helix minus the fraction that is a left-handed helix, as a function of r and p. This prediction can be done either through a numerical transfer-matrix calculation[36−38,44−46] or through an approximate analytic calculation.[36−38] The approximate analytic calculation depends on the relative magnitude of three parameters: the thermal energy RT, the helical domain size L along the chain, and the chiral bias ΔG_h, which represents the energetic preference of a chiral monomer to be in a right- or left-handed helix. If $\Delta G_h\ (Lr)^{1/2} \gg RT$, the polymer is in the limit of statistical randomness, that is, the dominant disorder in the chain arises from the random sequence of monomers. In this case, the theory predicts

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

By contrast, if $\Delta G_h\ (Lr)^{1/2} \ll RT$, the polymer is in the limit of thermal randomness, that is, the dominant disorder in the chain arises from thermal fluctuations of the local helical sense. In the Appendix (see below), the theory is extended to describe this case. The resulting prediction is

$$M = \tanh\left[\frac{2\Delta G_h Lr\left(p - \frac{1}{2}\right)}{RT}\right] \tag{2}$$

The distinction between statistical randomness and thermal randomness is very important for explaining how the excess helical sense M depends on the degree of polymerization. This dependence arises from the fact that the helical domain size L is limited by chain length as well as by statistical and thermal randomness in the chain. In general, the helical domain size can be written as $L = (N^{-1} + L_{\max}{}^{-1})^{-1}$, where N is the degree of polymerization and $L_{\max}$ is the limiting domain size for infinite chains. Inserting this expression into eqs 1 and 2, and expanding the erf and tanh functions for the small enantiomeric excess of a photoresolution experiment, gives

$$M = \frac{2^{3/2} r^{1/2}\left(p - \frac{1}{2}\right)}{\pi^{1/2}}\left(\frac{NL_{\max}}{N + L_{\max}}\right)^{1/2} \tag{3}$$

in the limit of statistical randomness and

$$\mathrm{M} = \frac{2\Delta G_h Lr\left(p - \frac{1}{2}\right)}{RT}\left(\frac{NL_{\max}}{N + L_{\max}}\right) \tag{4}$$

in the limit of thermal randomness. Note that these equations make very different predictions for how the excess helical sense should depend on N. In the limit of statistical randomness, eq 3 predicts that M should scale as $N^{1/2}$ for short chains and then saturate at a constant value for long chains. The coefficient of $N^{1/2}$ for short chains should be $2^{3/2}r^{1/2}(p - (1/2))/\pi^{1/2}$, which depends only on the composition of the chains, not on any energetic parameters. By contrast, in the limit of thermal randomness, eq 4 predicts that M should scale linearly with N for short chains and then saturate at a constant value for long chains. The coefficient of N for short chains should be $2\Delta G_h r(p - (1/2))/RT$, which depends on the energetic parameter ΔG_h as well as on the composition of the chains.

The experimental results for the molar ellipticity of the *ortho*-copolymer as a function of N, presented in Figure 9, show a clear curvature indicating the square-root behavior predicted for the limit of statistical randomness. To analyze the data, the molar ellipticity was normalized by the value of 52 000, corresponding to a chain with a single sense of helicity, to give the excess helical sense M. The resulting data for M were then fit to the prediction of eq 3, giving the solid line in Figure 9. The two parameters of the fit are $L_{\max} = 130$ and coefficient $2^{3/2}r^{1/2}(p - (1/2))/\pi^{1/2} = 5.5 \times 10^{-3}$. This value of $L_{\max}$ is similar to that of other (*R*)/(*S*) copolymers that have been studied.[36,37] Furthermore, because the chiral fraction is $r = 100\%$, the value of the coefficient implies that the ee of the *ortho* chiral pendants is $2(p - (1/2)) = 0.7\%$. Hence, this analysis provides an independent determination of the ee achieved through photoresolution, which confirms the value determined through spectroscopic techniques discussed above. Analogous data for the molar ellipticity of the *ortho*-terpolymer are presented in Figure 10. These results also show the square-root behavior predicted for the limit of statistical randomness, so that they were also fit to the prediction of eq 3, giving the parameters $L_{\max} = 6000$ and coefficient $2^{3/2}r^{1/2}(p - (1/2))/\pi^{1/2} = 6.1 \times 10^{-4}$. This value of $L_{\max}$ is consistent with that of other (*R*)/(*S*)/achiral terpolymers that have been studied.[38] Because the chiral fraction $r = 2\%$ in this terpolymer, the value of the coefficient implies that the enantiomeric excess is $2(p - (1/2)) = 0.6\%$. Again, this result agrees with the value of the ee determined independently (see above) through spectroscopic techniques.

The data for the molar ellipticity of the *meta*-copolymer, shown in Figure 11, appear quite different from the results for the ortho copolymer and terpolymer. For the *meta*-copolymer, the molar ellipticity scales linearly with N, not as the square root. This linear scaling agrees with the prediction for a polymer in the limit of thermal randomness. The data were normalized by the maximum value of 52 000 to give the excess helical sense M and then fit to the prediction of eq 4. In this fit, the parameter $L_{\max}$ is undefined because M scales linearly with N over the full range of N that was studied, so one can only conclude that $L_{\max} \gg 600$. The coefficient of the linear dependence is well defined with the value $2\Delta G_h r(p - (1/2))/RT = 7.8 \times 10^{-5}$. Using the thermal energy $RT = 600$ cal/mol at room temperature and the chiral fraction $r = 100\%$, and assuming that the ee of the *meta* chiral pendant is $2(p - (1/2)) = 1\%$ derived from the spectroscopic data discussed above, this coefficient implies that the chiral bias energy is $2\Delta G_h = 9$ cal/mol. This chiral bias energy is much smaller than that of most polyisocyanates that have been studied,[36,37,44−46] and it shows that the relation $\Delta G_h\ (Lr)^{1/2} \ll RT$ for thermal randomness is self-consistent. Presumably, the chiral bias of the *meta* unit is much smaller than that of the analogous *ortho* unit because the interaction of the chiral *meta*-bicyclic ketone pendants with the polymer backbone is much weaker than that of *ortho*-bicyclic ketone pendants.

The data for the *meta*-terpolymer in Figure 12 are the most difficult to analyze because they show a scaling that is intermediate between the linear and square root predictions. Apparently this polymer is not in the limit of either statistical randomness or thermal randomness but is in an intermediate regime between these two limits. To fit the data, the empirical interpolation function

$$M = \frac{1}{(1/aN) + (1/bN^{1/2}) + (1/c)} \tag{5}$$

was used. This interpolation function scales linearly with N for small N, then crosses over to $N^{1/2}$ for intermediate N, and finally saturates at a constant value for large N. In the fit, the coefficient of the $N^{1/2}$ dependence is fixed at $b = 2^{3/2}r^{1/2}(p - (1/2))/\pi^{1/2} =$

1.1×10^{-3}, using the known chiral fraction $r = 2\%$ and enantiomeric excess $2(p - (1/2)) = 1\%$. The fit then shows that the crossover from linear to square-root dependence occurs around $N \approx 1000$ and that the crossover from square-root dependence to saturation occurs around $N \approx 1400$. Furthermore, the fit gives the coefficient of the linear dependence $a = 2\Delta G_h r(p - (1/2))/RT = 3.3 \times 10^{-5}$. This coefficient implies that the chiral bias is $2\Delta G_h = 220$ cal/mol. All of the parameters derived from this fit have very large uncertainties because they depend sensitively on the value of the chiral fraction and the assumed value of the ee. However, the chiral bias derived for this *meta*-terpolymer is clearly much greater than the chiral bias of the *meta*-copolymer discussed above. The increase shows that surrounding the chiral *meta*-units with the achiral 2-butylhexyl units in the terpolymer has a very substantial effect on increasing the chiral bias of the *meta*-units to a level so that the degree of polymerization allows crossing over from thermal to statistical randomness. The detailed structural basis of this increase in chiral bias is not clear although this is an excellent example that the extent of chirality depends on the detailed structural environment and should not be considered an intrinsic property of the chiral entity.[47]

Conclusions

A series of polyisocyanates were prepared that consisted of varying proportions of a chiral, photoresolvable ketone-containing pendant group and an achiral alkyl group. When the chiral pendant group is racemic, both helical senses of the polyisocyanate backbone are equally populated, and there is no circular dichroism spectrum. Irradiation of the pendant ketone group with CPL results in its partial photoresolution. The majority rule effect transfers the chirality of the pendant group to the backbone of the polymer, resulting in amplification of the photoresolution. Depending on the details of the ketone's structure, the resolved pedant group has more (*ortho*), less (*meta*), or almost no (*para*) chiral bias (ΔG_h). The helical sense of the polymer may be switched reversibly by alternating irradiation with (+) or (−)CPL or returned to the racemic state by irradiation with plane polarized light. These effects can be understood quantitatively through application of a quenched random-field Ising model, which also details the parameters necessary for this kind of observation in other polymer or supramolecular helical systems with the prerequisite properties. This is the first demonstration of amplification of a photochemical resolution by the response of the conformation of a polymer backbone.

Experimental Section

General. Circular dichroism (CD) spectra were recorded on a JASCO 720 Spectropolarimeter. UV−vis spectra were recorded on a Cary 1E UV−vis spectrophotometer. Enantiomeric resolution by HPLC was performed on a Hitachi L-6200A Intelligent Pump with a L-4500A diode array plus As-4000 Intelligent Auto Sampler. A chiral WHELK-01 column (25 cm × 4.6 mm i.d., Regis Chemical Co.) was used. Gel permeation chromatography was performed using a Waters 510 pump and Waters 440 UV detector at 254 nm. Chloroform was used as a mobile phase on the following set of TSK-gel analytical columns: G4000H$_{XL}$ (10^4 Å pore size), G5000H$_{XL}$ (10^5 Å pore size), and GMH$_{XL}$-HT (1500−10^7 Å pore size), all 30 cm long and with an i.d of 7.8 mm connected in series, with a flow rate of 1.0 cm^3/min. The GPC instrument was calibrated at 30 °C with poly(*n*-hexyl isocyanate) standards samples kindly supplied from the laboratory of professor Akio Teramoto, Osaka University, Osaka, Japan. All solvents used for the irradiation and measurement for CD and UV were of spectrometric grade. The synthetic work will be described later.

Enantiomer Resolution of 6, 7, and 8 by Chiral HPLC. The enantiomers of **6**, **7**, and **8** were resolved by HPLC through WHELK-01 chiral column. The resolution conditions were as follows: room temperature, mobile phase [*n*-hexane: *tert*-butyl alcohol = 99:1 (v:v)], flow rate (1.0 mL/min) for compound **6**; mobile phase [*n*-hexane: *tert*-butyl alcohol = 99.76:0.24 (v:v)], flow rate (1.2 mL/min) for compound **7**; mobile phase [*n*-hexane: *tert*-butyl alcohol = 96.8:3.2 (v:v)], flow rate (2.1 mL/min) for compound **8**. The ee of the collected, optically active samples was determined by reinjection.

General Procedure for the Photoresolution of Model Compounds 6, 7, 8 and the Polymers Incorporated with the Bicycloketone Pendants. Circularly polarized light (CPL) was produced with a high pressure 1000 W Hg−Xe arc lamp. The light beam was first passed through a focusing lens and a 305 nm cutoff filter. Then, it was passed through an air-gap linear polarizer and finally a Fresnel rhomb. The formation of CPL was confirmed by photoresolution of (±)-**1**.[20] The handedness of the CPL was selected as (+) or (−) by a 90° rotation of the linear polarizer. The sample solutions were deoxygenated by purging with N_2 for 10 min before exposure to CPL. The irradiation time varied with the amount of the sample (typically 24 h). The progress of the reaction was monitored by CD spectroscopy.

GPC Copolymer and Terpolymer Fractionation. After irradiation with CPL the polydisperse copolymer and terpolymer samples were fractionated by gel permeation chromatography, using the conditions described above. In each case, 200 μL of the polymer sample (3 mg dissolved in 3 mL of $CHCl_3$) were injected. The fractionated samples were collected every 30 s starting 11 min after the injection. Molecular weights and polydispersities of the collected samples were determined by reinjection under the same chromatographic conditions. The solvents were evaporated by purging with Ar, and the samples were further dried in a vacuum oven overnight. The dried, fractionated samples were dissolved (solvents identified in Figure Captions), the concentration of the samples was determined by their absorption at 254 nm.

Appendix: Theoretical Distinction between Statistical and Thermal Randomness

Earlier theoretical papers made predictions for chiral order in (*R*)/(*S*) copolymers[36,37] and (*R*)/(*S*)/achiral terpolymers[38] in the limit of statistical randomness. The purpose of this Appendix is to derive the analogous predictions for chiral order in the limit of thermal randomness, and to compare these two limiting cases.

Chiral order in random heteropolymers can be described by the one-dimensional random-field Ising model. Let the variable σ_i represent the local sense of helicity at monomer *i*, with $\sigma_i = +1$ corresponding to one helical sense and $\sigma_i = -1$ corresponding to the opposite. The Hamiltonian for a polymer of length *N* can then be written as

$$H = -\frac{1}{2}\Delta G_r \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - \sum_{i=1}^{N} \Delta G_{h,i} \sigma_i \qquad \text{(A1)}$$

The first term in this Hamiltonian gives the energy cost of a helical 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*) unit has $\Delta G_{h,i} = +\Delta G_h$, an (*S*) unit has $\Delta G_{h,i} = -\Delta G_h$, and an achiral unit has $\Delta G_{h,i} = 0$. The random field $\Delta G_{h,i}$ is a quenched random variable, which is fixed by the polymerization of the chain and does not change in response to changes in the local helical sense σ_i.

The optical activity measured experimentally is proportional to the net excess of one helical sense over the opposite. This

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[47] Buda, A., B.; Auf der Heyde, T.; Mislow, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 989−1007. Lipkowitz, K. B.; Gao, D.; Katzenelson, O. *J. Am. Chem. Soc.* **1999**, *121*, 5559. For an experimental technique that can be used to quantitatively measure the extent of relative chirality, see: Cheon, K. S.; Selinger, J. V.; Green, M. M. *Angew. Chem. Int. Ed.*, in press.

net helical excess can be written theoretically as the chiral order parameter

$$M = \left\langle \frac{1}{N} \sum_{i=1}^{N} \sigma_i \right\rangle \tag{A2}$$

The goal of the theory is thus to calculate M for any statistical distribution of the (R), (S), and achiral units, as a function of their relative proportions, the temperature T, the chain length N, and the energetic parameters ΔG_r and ΔG_h. This calculation can be done at a high level of precision through a numerical approach, in which one constructs a particular realization of the random-field, calculates the expectation value of M by the transfer-matrix technique, and then averages over many realizations of the random field.[36−38,44−46] However, it is both convenient and instructive to do this calculation through an approximate analytic approach, which can give compact algebraic predictions for M.[36−38]

In the approximate approach, suppose that each polymer consists of domains of uniform helicity with a single characteristic domain size L, which is to be determined. Each domain responds to the total chiral field $\Delta G_{h,\mathrm{tot}} = \sum \Delta G_{h,i}$ of the monomers in it. Because the domain is uniform, the response to this chiral field is the thermal expectation value $M(\Delta G_{h,\mathrm{tot}}) = \tanh(\Delta G_{h,\mathrm{tot}}/RT)$. Averaging over the probability distribution $P(\Delta G_{h,\mathrm{tot}})$ gives

$$M = \int_{-\infty}^{\infty} d(\Delta G_{h,\mathrm{tot}}) P(\Delta G_{h,\mathrm{tot}}) \tanh\left(\frac{\Delta G_{h,\mathrm{tot}}}{RT}\right) \tag{A3}$$

The probability distribution $P(\Delta G_{h,\mathrm{tot}})$ depends on the statistical distribution of the (R), (S), and achiral units in the polymer. Consider an (R)/(S)/achiral terpolymer in which a fraction r of the monomers are chiral and a fraction p of the chiral monomers are (R). (An (R)/(S) copolymer is a special case in which $r = 1$.) The probability distribution $P(\Delta G_{h,\mathrm{tot}})$ is then a trinomial distribution (or a binomial distribution in the special case of an (R)/(S) copolymer). For large domains, it can be approximated by a Gaussian with mean $2\Delta G_h Lr(p - (1/2))$ and standard deviation $\Delta G_h\{Lr[1 - r + 4rp(1 - p)]\}^{1/2}$. For $p \approx 1/2$ near the racemic point, the standard deviation becomes $\Delta G_h(Lr)^{1/2}$. The integral of eq A3 can now be evaluated approximately in two distinct limiting cases:

(1) Statistical Randomness. If $\Delta G_h(Lr)^{1/2} \gg RT$, then the width of the Gaussian is much greater than the width of the tanh, and the tanh is effectively a step function. In this case, the polymer consists of domains with very different values of the total chiral bias $\Delta G_{h,\mathrm{tot}}$. Almost all domains with $\Delta G_{h,\mathrm{tot}} > 0$ have one helical sense, and almost all domains with $\Delta G_{h,\mathrm{tot}} < 0$ have the opposite. Hence, the main source of randomness in the polymer is the random sequence of monomers, rather than the thermal fluctuations in the response to a given sequence. For that reason, this can be described as the limit of "statistical randomness." This limit was treated in earlier theoretical papers,[36−38] which showed that

$$M = \mathrm{erf}\left[(2Lr)^{1/2}\left(p - \frac{1}{2}\right)\right] \tag{A4}$$

This result is consistent with earlier experiments on polyisocyanates.[29,35]

(2) Thermal Randomness. If $\Delta G_h(Lr)^{1/2} \ll RT$, then the width of the tanh is much greater than the width of the Gaussian, and the Gaussian is effectively a δ-function centered at the mean $\Delta G_{h,\mathrm{tot}} = 2\Delta G_h Lr(p - (1/2))$. In this case, the polymer consists of domains with similar values of the total chiral bias $\Delta G_{h,\mathrm{tot}}$, but these domains have a Boltzmann distribution of different responses to the chiral bias. Hence, the main source of randomness in the polymer is thermal fluctuations rather than the random sequence of monomers. For that reason, this can be described as the limit of "thermal randomness." In this limit, the net helical excess becomes

$$M = \tanh\left[\frac{2\Delta G_h Lr\left(p - \frac{1}{2}\right)}{RT}\right] \tag{A5}$$

This result has not been seen experimentally in earlier studies, but the experimental results above show that it occurs in the *meta*-copolymer investigated here.

The predictions of eqs A4 and A5 both involve the characteristic helical domain size L. The inverse domain size $1/L$ is determined by two contributions, the density $1/L_{\mathrm{max}}$ of helical reversals and the density $1/N$ of chains ends, which combine to give

$$\frac{1}{L} = \frac{1}{L_{\mathrm{max}}} + \frac{1}{N} \tag{A6}$$

Hence, the domain size is approximately equal to the chain length N for short chains, and it grows asymptotically to the maximum value of L_{max} for long chains. In the limit of statistical randomness, L_{max} can be expressed as $1/L_{\mathrm{max}} = 1/L_{\mathrm{rf}} + 1/L_{\mathrm{th}}$, where $L_{\mathrm{rf}} = (\Delta G_r/2\Delta G_h)^2$ is the random-field domain size and $L_{\mathrm{th}} = e\Delta^{G_r/RT}$ is the thermal domain size.[36−38] In the limit of thermal randomness, there is no such simple expression for L_{max}, although L_{th} does provide an upper limit for it. In either case, however, eq A6 shows how the domain size depends on chain length for short chains. Thus, the two limiting cases of statistical randomness in eq A4 and thermal randomness in eq A5 can be distinguished experimentally by measuring the optical activity as a function of chain length, as in the experiments presented above.

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