structure of the acetato complex is consistent with the formula [Ru$_2$(OAc)(3,6-tBu$_2$sq)$_2$(btpyan)]$^+$.

[8] The bis(ruthenium–hydroxo) complex was prepared as follows: triflic acid (100 μL) was added to a solution of [Ru$_2$(OAc)(3,6-tBu$_2$sq)$_2$(btpyan)](OAc) (150 mg, 0.11 mmol) in MeOH (10 mL), and the solution was stirred for 4 d at room temperature. After the addition of NaSbF$_6$, the solution was concentrated to 5 mL to give [Ru$_2$(OH)$_2$(3,6-tBu$_2$qui)$_2$(btpyan)](SbF$_6$)$_2$ as a violet powder (57% yield). ESI-MS: m/z: 659(M^{2+}); elemental analysis calcd for $C_{72}H_{72}N_6O_6F_{12}Ru_2Sb_2$: C 48.34, H 3.94, N 4.70; found: C 48.39, H 3.85, N 4.64; UV/Vis-NIR (in MeOH): $\lambda_{max} = 576$ nm (ε = 5700 M^{-1}cm^{-1}). The oxidation of the semiquinone ligand of [Ru$_2$(OAc)(3,6-tBu$_2$sq)$_2$(btpyan)]$^+$ to the quinone ligand of [Ru$_2$(OH)$_2$(3,6-tBu$_2$qui)$_2$(btpyan)]$^{2+}$ during the reaction may be caused by O$_2$.

[9] M. Kurihara, S. Daniele, K. Tsuge, H. Sugimoto, K. Tanaka, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 867.

[10] The rest potential (V_{rest}) is defined as $V_{rest} = E_{1/2} + \mathrm{R}T/n\mathrm{F}\ln([\mathrm{Ox}]/[\mathrm{Red}])$ (R: gas constant, T: temperature, n: number of electrons in redox reaction, F: Faraday constant, Ox: oxidized species, Red: reduced species). Thereby, the distribution of the oxidized and reduced complexes in solutions can be evaluated from the difference between V_{rest} and $E_{1/2}$.

[11] A solution of the bis(ruthenium–hydoroxo) complex in acetone was dropped on an ITO electrode by microsyringe, and dried at room temperature.

[12] The cyclic voltammogram was measured at 10 mV s^{-1} in an H$_3$PO$_3$/KOH buffer solution (0.5 M) using an ITO electrode modified with the bis(ruthenium–hydroxo) complex (1.2×10^{-8} mol per 2.0 cm^2) as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl reference electrode.

[13] Two compartment cells separated by a Nafion membrane were filled with an H$_3$PO$_4$/KOH buffer solution (1.0 M, 60 mL) and He gas was bubbled into the solution to remove O$_2$ from the aqueous phase. Controlled-potential electrolysis was performed with the ITO electrode modified with the bis(ruthenium–hydroxo) complex (1.0×10^{-7} mol per 10 cm^2) as the working electrode, a platinum plate (2.0 cm^2) as the counter electrode, and an Ag/AgCl reference electrode. Evolved dioxygen was determined by GC measurement.

[14] The complex was completely detached from the ITO electrode in 40 h under the controlled-potential electrolysis conditions at +1.7 V in H$_2$O.

Designing a Helical Polymer that Reverses its Handedness at a Selected, Continuously Variable, Temperature[**]

Kap Soo Cheon, Jonathan V. Selinger,* and Mark M. Green*

A new kind of stereochemical experiment only accessible with cooperative helical arrays has been designed by enforcing a competition between two *structurally different* nonracemic chiral molecules to control the helical sense of a polymer. The experiment, which has been analyzed by a statistical physical theory, allows the optical activity of the polymer, as a function of the composition of the competing units, to be set to zero at any temperature and then increases in magnitude, in a positive or negative direction, as the temperature deviates from the chosen value.

Since the polyisocyanates[1] have served as models for other helical systems,[2] a conformational state of considerable interest,[3] we have applied this idea by synthesizing the polymer from structurally different chiral units, which compete with each other favoring the left- and right-handed helical senses. Since the strength of the chiral biases of the competing units for their favored helical sense are different, they compensate each other at some relative proportion away from 50/50. Moreover, since the competing chiral biases depend on temperature in different ways, this compensation point also depends on temperature. Hence, a polymer of fixed composition can pass through the compensation point as a function of temperature, with its dominant helical sense switching between left- and right-handed. This phenomenon can be described theoretically by a variation of the one-dimensional random-field Ising model.[4]

Three monomer units (**1**–**3**) were used in this study.[5] Homopolymers synthesized entirely from the *R* enantiomers of **1**, **2**, and **3** show identical circular dichroism spectra in sign and form, thereby demonstrating a preference for the same helical sense.[6] This corresponds to a negative rotation at the sodium D line.[1, 5, 6]

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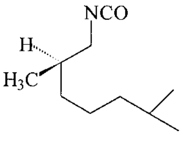
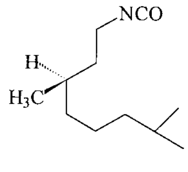
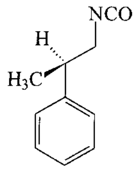
The competition for helical sense was designed through the synthesis of copolymers with various compositions of the following pairs: (*R*)-**1** and (*S*)-**3**; (*R*)-**2** and (*S*)-**1**. Figures 1 and 2 show the optical activity [α] as a function of temperature for the two sets of variable-composition copolymers.[7] In each of these cases, the optical activity is zero at a temperature ("compensation temperature") dependant upon the composition of the polymer; this is consistent with the reversal of the helical sense.[6] Although it is apparent from the data that the compensation point can be varied by simply changing the proportions of the competing chiral units in each polymer, the detailed response of the optical activity to composition and temperature differs greatly between the two systems. This difference can be understood in terms of the statistical physical theory discussed below.



(*R*)-**1**



(*R*)-**2**



(*R*)-**3**

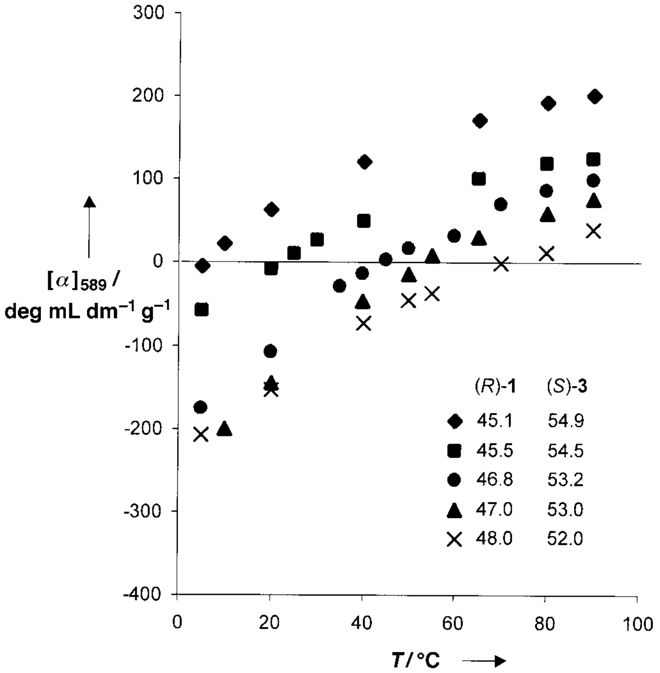


Figure 1. Optical activity [α] (at 589 nm) in a dilute toluene solution of the (*R*)-**1**/(*S*)-**3** copolymer as a function of temperature. ◆: $M_w = 48200$, polydispersity $\rho = 1.7$; ■: $M_w = 46800$, $\rho = 1.9$; ●: $M_w = 42300$, $\rho = 1.9$; ▲: $M_w = 219000$, $\rho = 2.4$; × : $M_w = 45100$, $\rho = 2.0$. Measurements are described in ref. [7].

The copolymers are described by adapting a random-field Ising model previously developed for copolymers synthesized from nearly racemic monomers.[4, 8, 9] This random field takes the values of $+\Delta G_{h1}$ for one type of chiral unit along the chain, $-\Delta G_{h2}$ for the competing chiral unit, and zero for any achiral units. The predictions of the theory can be derived by an approximate analytic solution that is a straightforward generalization of the solution for polymers with mirror-image units.[4, 8]

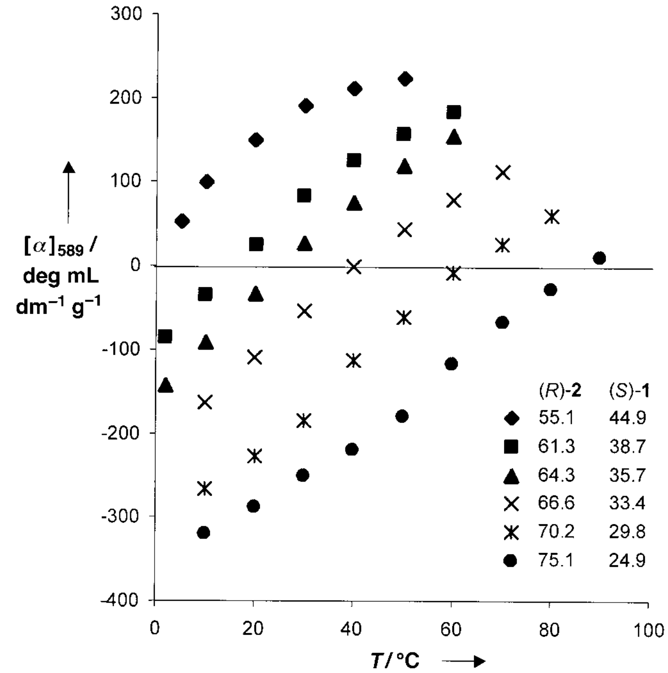


Figure 2. Optical activity [α] (at 589 nm) in dilute solution, in hexane for the four lowest temperatures and in octane for the two highest temperatures, of the (*R*)-**2**:(*S*)-**1** copolymer as a function of temperature. ◆: $M_w =$ 346000, $\rho = 2.9$; ■: $M_w = 269000$, $\rho = 2.8$; ▲: $M_w = 282000$, $\rho = 2.6$; ×: $M_w = 236000$, $\rho = 2.5$; ✱: $M_w = 300000$, $\rho = 2.7$; ●: $M_w = 290000$, $\rho =$ 2.5. Measurements are described in ref. [7].

Let r be the fraction of all monomer units that are chiral, and let p be the fraction of chiral units that are of type 1. The optical activity is then predicted by Equation (1), where $[\alpha]_{max}$ is the optical activity of a polymer with a single helical sense, *erf* is the standard error function of statistics, L is the helical domain size or correlation length along the chain, and p^* is given by Equation (2).

$$[\alpha] = [\alpha]_{max} erf\left[\sqrt{\frac{L\,r}{2p^*(1-p^*)}}(p-p^*)\right] \tag{1}$$

$$p^* = \frac{\Delta G_{h2}}{\Delta G_{h1} + \Delta G_{h2}} \tag{2}$$

In deriving this prediction, we assume that the sequence of units along the chain is random (see below) and that the statistical disorder in the random field exceeds the thermal energy, $(\Delta G_{h1} + \Delta G_{h2})\sqrt{2\,L\,r\,p^*(1-p^*)} \gg RT$. Both of these assumptions are justified in the systems studied earlier, and we expect them to apply in this case.

In the prediction of Equations (1) and (2), note that $p = p^*$ defines the compensation point at which the contributions of the competing chiral monomers cancel and the optical activity equals zero. For a polymer composed of mirror-image R and S units, we have $\Delta G_{h1} = \Delta G_{h2}$ by symmetry and hence $p^* = 1/2$ independent of temperature. However, for a polymer composed of competing chiral units that are not mirror images, p^*

is not ½. Moreover, the two chiral biases ΔG_{h1} and ΔG_{h2} will generally vary as functions of temperature and hence p^* will also vary as a function of temperature, $p^*(T)$. Therefore, the optical activity will vanish as a function of temperature when $p^*(T)$ passes through p, the fraction of chiral units that are of type 1. The compensation temperature can therefore be tuned continuously by varying the composition of the polymer, as seen in the experimental data in Figures 1 and 2.

The theory yields further insight into the experimental results. Consider the relationship between compensation temperature and composition shown in Figure 3.

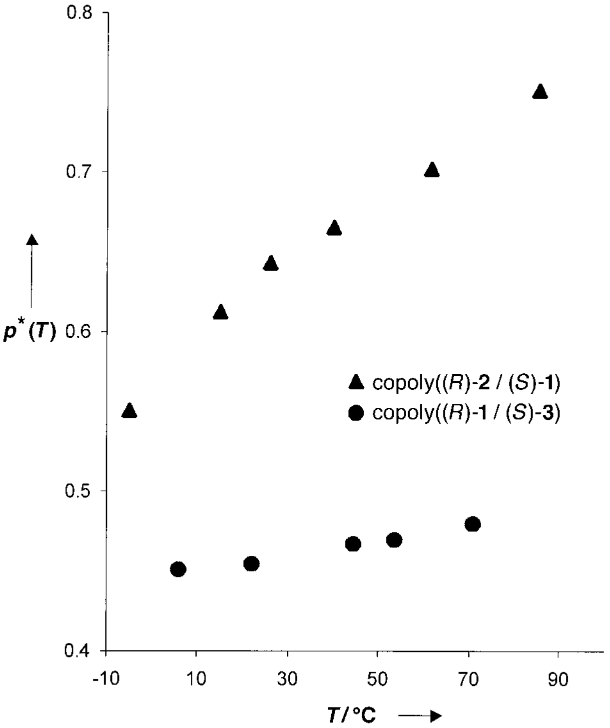


Figure 3. Relationship between composition and temperature at the compensation point for all the copolymers exhibited in Figures 1 and 2.

Equation (2) shows that changes in $p^*(T)$ with temperature correspond to changes in the ratio of the temperature-dependant chiral-bias free energies $\Delta G_{h1}(T)$ and $\Delta G_{h2}(T)$. If this ratio of free energies changes rapidly with temperature, then $p^*(T)$ also changes rapidly too, and hence a small change in compensation temperature will correspond to a large change in composition. Conversely, if this ratio of free energies changes slowly as a function of temperature, then a large change in compensation temperature will correspond to a small change in composition. The free energy dependence on temperature is primarily associated with entropy, which is linked to the flexibility of the chiral units. This is consistent with the greater slope of the data shown in Figure 3 with copolymers with **2** rather than **3**.[10]

Another feature of the experimental data is in $d[\alpha]/dT$ around the compensation temperature. The theory predicts Equation (3).

$$\frac{d[\alpha]}{dT}[p = p^*(T)] = -[\alpha]_{\max}\sqrt{\frac{2Lr}{\pi p^*(1-p^*)}}\,\frac{dp^*}{dT} \qquad (3)$$

This equation implies that the slope $d[\alpha]/dT$ is proportional to the slope dp^*/dT, with a proportionality constant that depends on the cooperative length scale L. A comparison of the slopes found in Figures 1 and 2 with Figure 3 confirms that the slopes are correlated. However, the observed slope $d[\alpha]/dT$ is not quite as large as predicted by the theory. For example, consider the copolymer (*R*)-**2**/(*S*)-**1**. With the chiral fraction $r = 1$, the maximum optical activity is approximately $[\alpha]_{\max} \approx -500°\,\mathrm{mL\,dm^{-1}\,g^{-1}}$,[1] and the slope in Figure 3 is approximately $dp^*/dT \approx 0.002\,\mathrm{K^{-1}}$. Based on earlier experiments with copolymers of mirror-image chiral units, we expect the helical domain size to be at least $L = 100$. To test this expectation, we have used gel-permeation chromatography to fractionate one of these copolymers into a number of narrow molecular mass samples.[11] Figure 4 confirms that the molar ellipticity θ of the fractionated samples depends on chain length for a degree of polymerization N of up to several hundred monomer units, which is consistent with L of order at least 100. Hence, the slope $d[\alpha]/dT$ should be at least $16°\,\mathrm{mL\,dm^{-1}\,g^{-1}\,K^{-1}}$ [Eq. (3)]. However, the experimental slopes around the compensation temperature in Figure 2 are only $d[\alpha]/dT \approx 5.7°\,\mathrm{mL\,dm^{-1}\,g^{-1}\,K^{-1}}$.

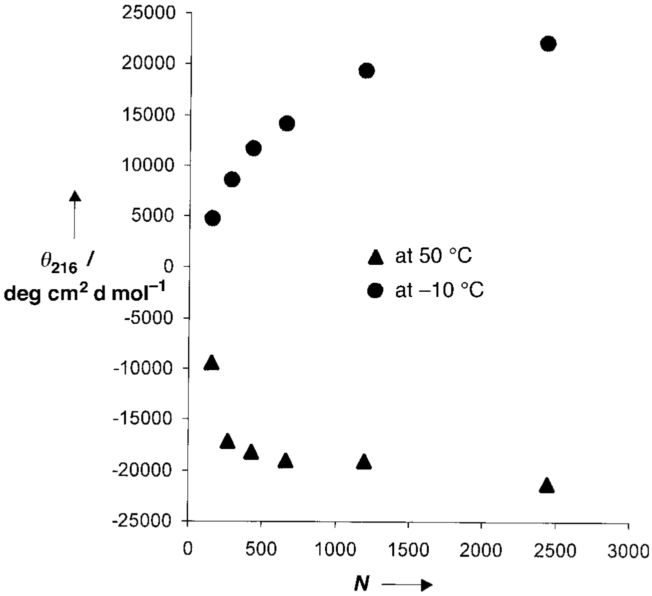


Figure 4. Molar ellipticity θ (at 216 nm) as a function of the degree of polymerization N (chain length) for the fractionated copolymer (*R*)-**2**/(*S*)-**1**.

Since any deviation from randomness[12] in the copolymerization could led to a reduction in $d[\alpha]/dT$,[8] we have studied this factor by degrading one composition of each copolymer to trimers. The composition of trimer population, determined by NMR, can reveal the microstructure, as has been described.[12a] The data show the copolymerizations to be so near to random as to exclude this as an explanation for the discrepancy in compared slopes noted above.[13]

Figures 1 and 2 also show the optical activity is more sensitive to temperature below, rather than above, the compensation point. This can be understood since the helical domain size L, on which the optical activity depends [Eq. (1)], itself depends on temperature.[1] Indeed, Figure 4 shows explicitly that the optical activity saturates for shorter chain length at 50 °C than at −10 °C, confirming that L is shorter at high temperature than at low temperature.

In conclusion, we have designed a polymer in which structurally different chiral units compete to control the helical sense of the polymer chain. This competition leads to thermal switching of the helical sense at a compensation point that depends continuously and predictably on the composition of the polymer. This model effect,[14] potentially applicable to other macromolecular and supramolecular helical systems, and which can be understood in terms of a theory of cooperative helical order, may offer new materials based on liquid crystals[15] in which the changes in the chiral characteristics of the polymer can translate into conversions between a nematic state and cholesteric states of opposite sense.

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[7] Polymerization of the copolymers were carried out by the routine NaCN/DMF method. For leading references see ref. [1]. Weight-averaged molecular masses M_w and polydispersities ρ of the polymers were determined by gel-permeation chromatography using poly(*n*-hexyl isocyanate) standards. The optical activity–temperature dependence of the polymer, to be reported in a full paper to follow, were studied in various solvents and the slope of the $[\alpha]_{589}$ versus T graph was strongly affected by the solvent. Experiments in the solvents reported in Figures 1 and 2 showed the steepest $[\alpha]_{589}$ versus T slopes.

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[11] The polydisperse copolymer sample was fractionated as described in earlier work.[9]

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