

## Transfer of Chirality from Circularly Polarized Light to a Bulk Material Property: Propagation of Photoresolution by a Liquid Crystal Transition

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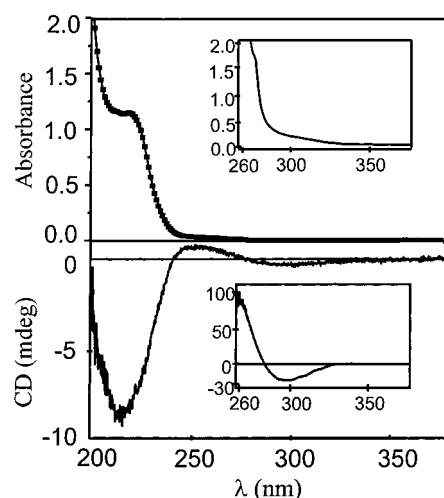
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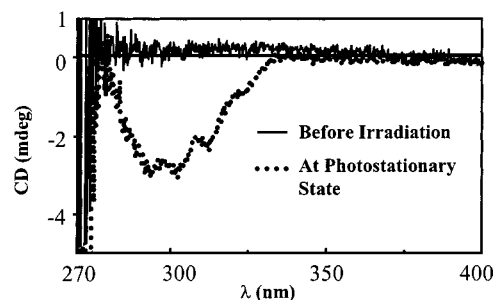
The properties of materials can be controlled remotely by light-driven reactions.<sup>1,2</sup> A unique aspect of photochemistry is that a key reagent, light, is generated externally and then can be directed to a particular location within a reaction vessel. Information storage by photography, for example, exploits this feature. The four controllable properties of light are its intensity, wavelength, speed, and polarization. The first three are routinely used to control reaction location or specificity; the fourth is rarely used.<sup>3</sup> We have developed light-driven reactions whose outcome depends on polarization.<sup>4–6</sup> Irradiation of the racemic form of a chiral bicyclic ketone (the trigger) with circularly polarized light (CPL) results in its partial photoresolution; irradiation with unpolarized light reverses this process. We report herein the first direct measurement of the reversible transfer of chirality from CPL to a bulk material property.

Light-driven control of liquid crystal materials is an area of extensive investigation.<sup>7</sup> Typically, the isomerization of a photochromic compound is used to modify the phase or thermal properties of these materials, which is an example of wavelength control.<sup>8–22</sup> A unique feature of liquid crystals is that addition of a small amount of an optically active substance will induce the formation of a bulk chiral phase.<sup>23,24</sup> Thus, photoresolution of a dissolved racemic trigger with CPL can induce the conversion of a liquid crystal from its nematic to cholesteric form; irradiation with unpolarized light would then regenerate the nematic phase. The challenge in accomplishing this goal has been the discovery of trigger compounds that simultaneously satisfy four critical parameters. The trigger must be chiral, thermally stable, and

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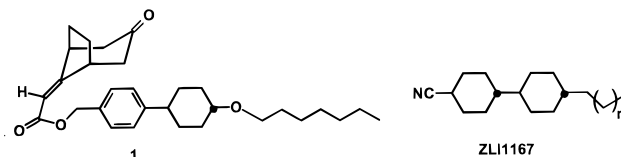


**Figure 1.** UV absorption and CD spectra of trigger (+)-**1** in MCH solution in a 0.1 cm path length cell with a concentration of 7.0 mM. Inset: 1.0 cm path length cell with a concentration of 9.9 mM.



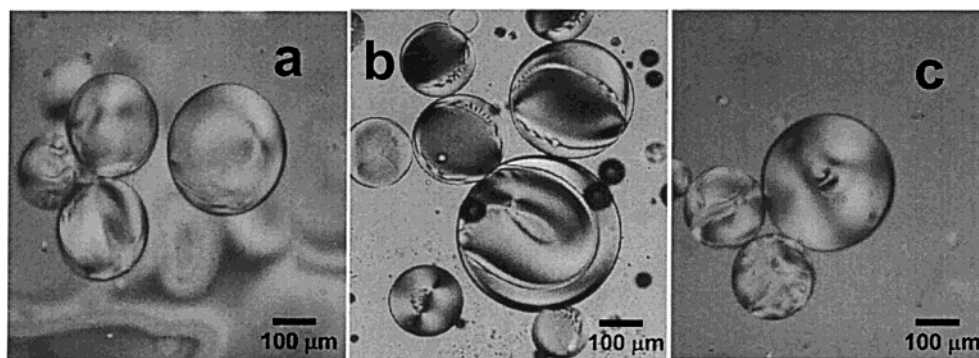
**Figure 2.** Circular dichroism spectra of **1**, before and after irradiation of a racemic sample with circularly polarized light.

reversibly resolvable photochemically to sufficient enantiomeric excess ( $[\gamma]$ ), and have a twisting power ( $\beta_M$ ) great enough to yield an observable chiral phase. The acrylic ester-substituted bicyclic ketone (**1**) is the first compound that satisfies these requirements. A cholesteric phase is induced in droplets of the liquid crystal ZLI1167 (a mixture of 4-cyano-4'-*n*-alkylbicyclohexanes) by irradiation of ( $\pm$ )-**1** with CPL.



The synthesis of resolved **1** was carried out using standard procedures and its characterization is provided as Supporting Information. There are two essential components to the structure of **1**: the bicyclic ketone and the acrylic ester. We have shown previously that the  $n\pi^*$  absorptions of related bicyclic ketones have low extinction coefficients and high  $\Delta\epsilon$  values (ca. 0.5–1  $M^{-1} cm^{-1}$ ).<sup>4–6</sup> These are the key parameters that determine the enantiomeric excess reached at the photostationary state,  $[\gamma]_{PSS}$ , by irradiation with CPL (eq 1).<sup>25</sup> The UV-absorption and CD spectra of (+)-**1** in methylcyclohexane (MCH) solution are shown in Figure 1. The absorption spectrum shows a weak  $n\pi^*$  band at wavelengths  $>300$  nm. The circular dichroism (CD) spectrum of (+)-**1** shows a negative Cotton effect at 300 nm. From these spectral data, the calculated maximum  $[\gamma]_{PSS}$  obtainable for **1** is 0.8%.

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**Figure 3.** Photomicrograph of trigger **1** dissolved in ZLI1167 dispersed as droplets in glycerol: (a) nematic phase before irradiation; (b) cholesteric phase after irradiation of ( $\pm$ )-**1** with CPL; and (c) nematic phase after irradiation of a sample with unpolarized light.

$$[\gamma]_{\text{pss}} = \Delta\epsilon/2\epsilon \quad (1)$$

The photostability, photoracemization, and photoresolution of **1** were examined under conditions simulating that of its irradiation in a liquid crystalline environment (see the Supporting Information). Racemic **1** is thermally and photochemically stable. A  $\text{N}_2$ -saturated MCH solution (11.7 mM) of ( $\pm$ )-**1** is unchanged when irradiated at  $\lambda > 295$  nm either at room temperature or at 85 °C. The enantiomers of **1** are interconverted by rotation about the double bond of the acrylic ester group. Irradiation of a MCH solution of (+)-**1** at  $\lambda > 295$  nm results in its racemization, as monitored by measuring the change in its CD spectrum at 300 nm. The quantum yield for photoracemization ( $\Phi_{\text{rac}}$ ) is  $0.39 \pm 0.05$ , revealing an efficient process since the maximum value of  $\Phi_{\text{rac}}$  is 0.5. Evidently, light absorbed by the carbonyl group of **1** forms the excited singlet state, which is expected to intersystem cross rapidly to the triplet state. Intramolecular, exothermic energy transfer yields the acrylic acid triplet state where the isomerization occurs.<sup>26</sup>

Since  $\Delta\epsilon \neq 0$ , the enantiomers of **1** absorb CPL with different probabilities. A photostationary state will be formed when the two enantiomers reach the same absorbance:  $(\epsilon^{\lambda}_{(+)\mathbf{1}})[(+)\mathbf{1}] = (\epsilon^{\lambda}_{(-)\mathbf{1}})[(-)\mathbf{1}]$ . Figure 2 shows the CD spectrum obtained after irradiation of a 21 mM MCH solution of ( $\pm$ )-**1** with CPL ( $\lambda > 295$  nm, room temperature) to the stationary state. This experiment gives  $[\gamma]_{\text{pss}} = 0.7\%$ , which is within experimental error of the calculated value. Similar results are obtained at 85 °C, and an equal but oppositely signed CD spectrum is obtained when the handedness of the CPL is reversed. Clearly, irradiation of ( $\pm$ )-**1** with CPL results in its predicted partial photoresolution.

The second essential element in the design of **1** is the alkyl group of the acrylic ester. The trigger's chirality is transferred to the liquid crystal through molecular scale interactions;  $\beta_{\text{M}}$  is a measure of their effectiveness. It is generally found that triggers whose overall structures resemble that of its liquid crystal host give larger  $\beta_{\text{M}}$  values.<sup>27–29</sup> We explored a range of alkyl groups and a few liquid crystalline materials that are transparent at  $\lambda > 295$  nm to find a high  $\beta_{\text{M}}$  value. This survey showed that the derivatives with the highest  $\beta_{\text{M}}$  had a rod-shaped component, such as a bicyclohexyl or phenylcyclohexyl group, linked to the ester through at least one methylene group, and an appended long-chain alkoxy group to increase solubility. The  $\beta_{\text{M}}$  for **1** in ZLI1167 was determined to be  $15 \mu\text{m}^{-1} \text{mol}^{-1}$  by observing liquid crystal droplets suspended in glycerol microscopically between crossed polarizers. The cholesteric phase gives a spiral shaped pattern with a radial disclination. The distance between two consecutive rings is half the helical pitch ( $p$ ).<sup>30</sup>

The transition temperatures for ZLI1167 containing 13 mol % (+)-**1** were measured by differential scanning calorimetry. Smectic–nematic and nematic–isotropic transitions were observed at 16.3 °C ( $\Delta H = 3.57$  J/g) and 61.7 °C ( $\Delta H = 3.36$  J/g), respectively. No phase separation was observed at this concentration. A mixture consisting of 13 mol % of ( $\pm$ )-**1** dissolved in ZLI1167 suspended as mechanically formed droplets in glycerol at 70 °C was irradiated with CPL ( $\lambda > 295$  nm). Aliquots were removed at various intervals and directly analyzed microscopically. Before irradiation, the droplets showed a pattern characteristic of a nematic phase, Figure 3a. After irradiation with CPL, the droplets show a pattern characteristic of a cholesteric liquid crystal, Figure 3b. The helical pitch of the irradiated droplets determined by direct microscopic observation is  $190 \pm 5.5 \mu\text{m}$ . The light-induced cholesteric droplets are stable as long as they are not exposed to UV light. But their irradiation with unpolarized light ( $> 295$  nm, 70 °C) results in reformation of the nematic phase, Figure 3c. This is the first direct measurement of a bulk material property controlled directly by light in a polarization-dependent chemical reaction.

The magnitude of  $p$  is inversely proportional to  $[\gamma]_{\text{pss}}$ ,  $\beta_{\text{M}}$ , and the concentration of trigger ( $c$ , in mol %) according to eq 2. The value of  $p$  expected from irradiation of 13 mol % ( $\pm$ )-**1** in ZLI1167 is  $73 \mu\text{m}$ . We obtained  $p = 88 \mu\text{m}$  when a sample of photoresolved **1** (13 mol %) is added to ZLI1167. The value of  $p$  is ca. two times larger when the irradiation is carried out in the liquid crystal material. The origin of this difference remains to be determined, but it may be due to the quality of the CPL in the scattering environment of the droplet mixture.

$$p = ([\gamma]_{\text{pss}} c \beta_{\text{M}})^{-1} \quad (2)$$

In summary, these experiments demonstrate reversible control of the chirality of a liquid crystal material by modulation of the polarization of light irradiating a dissolved trigger. The differential absorption properties of the trigger are translated through a photoisomerization reaction into an enantiomeric excess. The properties of the liquid crystalline material are switched by this trigger between nematic and cholesteric forms. These features may be useful for the development of light-controlled devices.

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**Supporting Information Available:** Synthesis and characterization of **1** and description of the droplet method and of the photoresolution procedure (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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