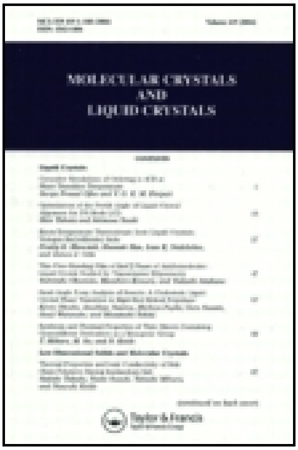

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Chiral Supramolecular Materials from Columnar Liquid Crystals

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CHIRAL SUPRAMOLECULAR MATERIALS FROM COLUMNAR LIQUID CRYSTALS

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Chirality plays an integral role in the molecular organization of many liquid crystals and, consequently, in the design of liquid crystal-based supramolecular materials. Chiral columnar phases are of particular interest since they can serve as synthetic templates for polymer networks with helical channels or pores. Several β*-diketonate ligands have been synthesized to contain a chiral directing element and/or a polymerizable moiety. Octahedral iron complexes of these ligands were crosslinked in the columnar hexagonal phase using acyclic diene metathesis (ADMET) polymerization. The resulting materials were chiral and retained the order of the mesophase.*

Keywords: acyclic diene metathesis polymerization; chirality; columnar hexagonal phase

Mesomorphic organizations represent the most powerful and efficient method for the preorganization of molecules to create nanometer-scale ordered synthetic systems. The incorporation of polymerizable groups within a liquid crystalline template is effective for the creation of anisotropic molecular networks [1]. We previously demonstrated the cooperative chiral ordering of octahedral metal complexes in columnar liquid crystals [2]. Building upon this system, we are developing methods to create robust, polymeric materials with intrinsically chiral pores or channels, with an eye toward asymmetric catalysis and chiral separation technologies. Although certain inorganic materials have been synthesized containing helical channels, there has been little success in controlling the chirality during synthesis and the resulting materials are racemic [3]. However, it is well known that small chiral perturbations in liquid crystalline phases, arising from either a chiral dopant or from the mesogen itself, can induce a strong, cooperative chiral response in the mesophase [4]. Taking advantage of the

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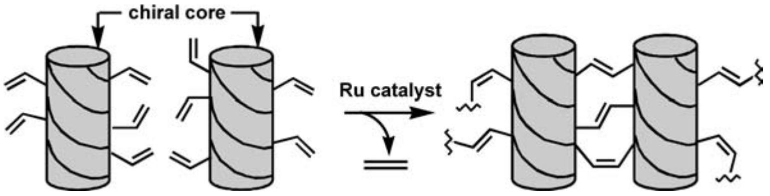
cooperative chirality exhibited by certain thermotropic liquid crystals, we have prepared chiral supramolecular materials using acyclic diene metathesis [5] (ADMET) polymerization as a means of crosslinking. (Scheme 1)



SCHEME 1 ADMET polymerization of a chiral columnar liquid crystal.

In the synthesis of chiral anisotropic networks, the polymerizable group should undergo rapid and efficient crosslinking with minimal perturbation of the liquid crystalline phase. Photo-polymerization of liquid crystals using either acrylate or 1,3-diene tails has been well established as a reliable method of synthesizing anisotropic materials with hexagonally ordered, hydrophilic pores [1,6]. Herein we describe the incorporation of terminal olefins within a liquid crystalline monomer and the use of ADMET polymerization to crosslink with retention of the original mesophase order. This approach is particularly attractive since the olefin crosslinking groups closely resemble typical alkyl side chains of the mesogens in size, hydrophobicity, and thermal stability, yet are reactive towards olefin metathesis. Another advantage of this method is that terminal olefins require shorter syntheses than acrylates and terminal 1,3-dienes, as bromoalkenes of various chain lengths are commercially available.

Liquid crystalline transition metal complexes previously studied by our group have provided the basis for our synthesis of chiral polymer networks. One such system focuses on the octahedral iron(III) complex **1**, [2,7] which forms columnar hexagonal phases (Fig. 1). The chiral side chains of **1a-b**

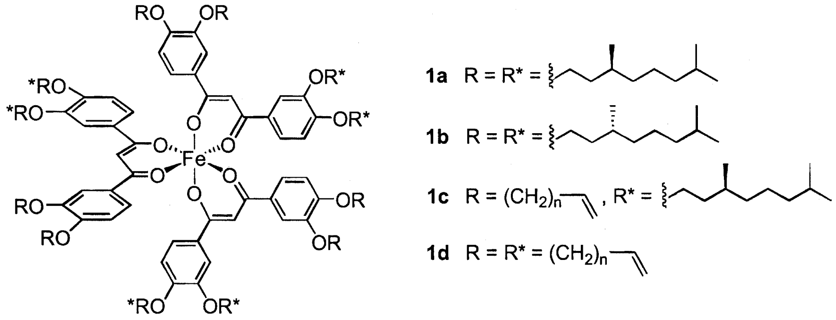
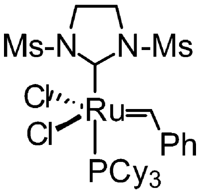


FIGURE 1 Octahedral iron complexes.

provide enough perturbation in the liquid crystal phase to favor one optical isomer (Λ or Δ) and to effectively induce helicity within a given column [8]. Simple side chain alteration of these mesogens provides the liquid crystalline monomers **1c-d** needed to prepare chiral supramolecular materials. The phase behavior is summarized in Table 1.

Under nitrogen atmosphere, solutions of **1c** and the Grubbs' catalyst **2** (1.0 mol% catalyst) in hexane are spin cast onto quartz plates, annealed to 90°C to order the mesophase, and then cooled to room temperature. Placing the films under vacuum for 24 hours results in a heavily crosslinked free-standing film, which is then rinsed with hexanes to remove any un-crosslinked material.



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Circular dichroism (CD) confirms that the post-polymerization films retain their chiral structure (Fig. 2). The X-ray diffraction (XRD) pattern shows slightly reduced peak intensities (Fig. 3) but indicates that the columnar hexagonal organization remains intact upon crosslinking. The reduction in lattice spacing is expected due to the net reduction in side chain lengths resulting from the expulsion of ethylene. Table 2 lists the XRD lattice constants of the hexagonal phases, before and after cross-linking.

TABLE 1 Phase Behavior of **1c** and **1d** [9]. The Transition Temperatures and the Enthalpies (in Parentheses) are given in °C and kcal mol^{-1}, Respectively, and were Determined by Differential Scanning Calorimetry (10 K min^{-1})

	Phase behavior
1a [9]	$\mathrm{Col_h} \underset{73.8(-2.1)}{\overset{81.0(2.1)}{\rightleftharpoons}}$ 1
1b [9]	$\mathrm{Col_h} \underset{76.5(-2.4)}{\overset{83.8(2.4)}{\rightleftharpoons}}$ 1
1c	$\mathrm{Col_h} \underset{54.0(-1.1)}{\overset{62.4(1.1)}{\rightleftharpoons}}$ 1
1d	$\mathrm{Col_h} \underset{61.0(-7.6)}{\overset{68.8(7.5)}{\rightleftharpoons}}$ 1

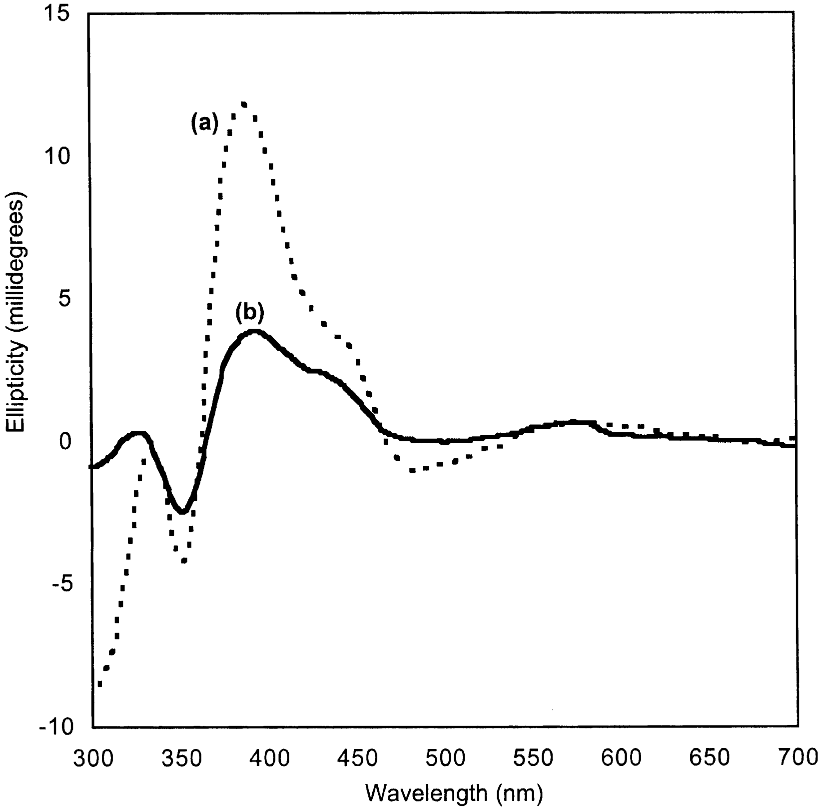

FIGURE 2 Circular dichroism of **1c**: (a) before polymerization and (b) after polymerization.

Complex **1d** was also crosslinked as described above. Furthermore, to introduce porosity into the materials **1d** was crosslinked using varying amounts of **1a** or **1b** as a chiral dopant. The crosslinked materials were rinsed with hexanes to wash away the chiral dopant, affording a porous material. XRD profiles resemble those shown in Figure 3 in which the peak intensity is slightly diminished upon crosslinking, yet the hexagonal phase is clearly retained. Table 3 lists the XRD spacing of the un-crosslinked and crosslinked hexagonal phases of achiral **1d**, as well as representative XRD spacing of the un-crosslinked and crosslinked hexagonal phases of chirally-doped **1d**. Again, circular dichroism confirms the chirality of the polymerized network. Studies are in progress to further characterize the porosity of these chiral crosslinked materials.

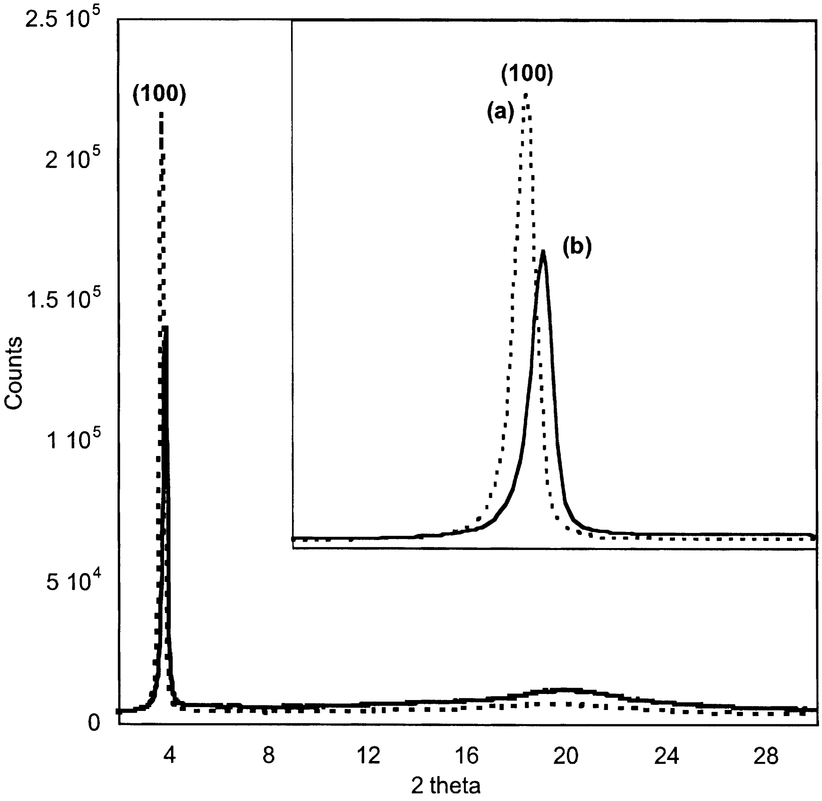

FIGURE 3 X-ray diffraction profiles of **1c**: (a) before polymerization and (b) after polymerization.

TABLE 2 X-ray Diffraction Data for **1c** Before and After Crosslinking

	Lattice constant (Å)	Spacing observed (Å)	Miller indices
1c (Before crosslinking)	26.9	23.3	(100)
		13.5	(110)
		4.49	halo
1c (After crosslinking extraction)	26.1	22.6	(100)
		13.4	(110)
		4.45	halo

TABLE 3 X-ray Diffraction Data for **1d** Before and After Crosslinking

	Lattice constant (Å)	Spacing observed (Å)	Miller indices
1d (Before crosslinking)	28.3	24.5	(100)
		4.18	halo
1d (After crosslinking extraction)	28.3	24.5	(100)
		4.29	halo
1d + chiral dopant (30 mol%) (Before crosslinking)	29.4	25.5	(100)
		4.44	halo
1d + chiral dopant (30 mol%) (After crosslinking)	27.8	24.1	(100)
		4.39	halo

In summary, we have demonstrated that the use of liquid crystallinity and ADMET polymerization is a viable and attractive route towards the synthesis of supramolecular polymeric materials. Retention of the ordered liquid crystal phase is achieved and we have utilized this method to synthesize several chiral polymer networks.

EXPERIMENTAL SECTION

General Methods

All chemicals were of reagent grade and were purchased commercially and used as received, unless otherwise specified. Tetrahydrofuran was dried by passing through activated alumina columns. The *bis*-1,3-(3′,4′-dialkoxyphenyl)-propanedione ligands were synthesized by condensation of the 3,4-dialkoxy ethyl benzoates with the corresponding 3,4-dialkoxy methyl ketones using the same procedures previously reported for related β-diketones [10], using commercially available 10-bromoundecene and (*S*)-(+)-citronellyl bromide as the alkyl bromides. (*S*)-(+)-citronellyl bromide was purchased from Aldrich (>99% purity) and was hydrogenated using literature procedures [11].

Transition temperatures and heats of fusion were determined at scan rates of 10°C/min by differential scanning calorimetry using a Perkin Elmer DSC-7 with a Perkin Elmer 7700 thermal analysis data station. Optical microscopy was performed on a Leica polarizing microscope in combination with a Mettler FP 80HT/FB 82HT hot stage. Spin cast films were made on quartz plates using a Laurell Spin Processor WS-400-6NPP-LITE at 500 rpm. X-ray diffraction studies were carried out on samples on aluminum plates with an INEL diffractometer with a 2 kW Cu K-a X-ray source fitted with an INEL CPS-120 positive-sensitive detector. The detector was calibrated using a silver behenate standard which was produced by

Eastman Kodak and supplied by The Gem Dugout. Circular dichroism spectra of spin cast films on quartz plates were recorded using an Aviv Model 202 Circular Dichroism Spectrometer.

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