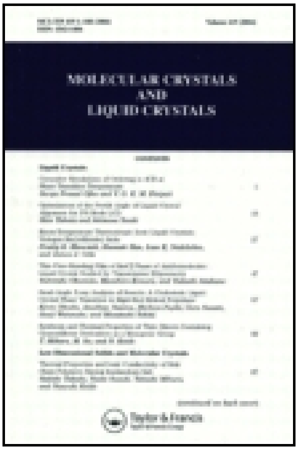

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# Synthesis and Polymerization of a Chiral Liquid Crystal Diacrylate Exhibiting Smectic A* and C* Phases

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# Synthesis and Polymerization of a Chiral Liquid Crystal Diacrylate Exhibiting Smectic A* and C* Phases

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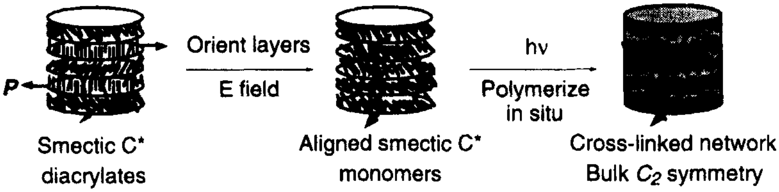
The alignment and cross-linking of chiral liquid crystal (LC) phases has been used to generate ordered noncentrosymmetric polymer networks with a variety of interesting optical and transducer properties. Examples of intrinsically chiral LC diacrylates which exhibit chiral smectic phases are rare because of the difficulties associated with the design of such monomers. We are presenting the stereospecific synthesis and subsequent photopolymerization of a chiral smectic diacrylate which is derived from (*S*)-ethyl lactate. This monomer exhibits an enantiotropic smectic A* phase from 49 to 71 °C upon heating at 0.5 °C/min and from 71 to 39 °C upon cooling at the same rate. The smectic A* phase of the chiral monomer can be homeotropically and homogeneously aligned and subsequently photopolymerized to yield highly uniform, noncentrosymmetric polymer films of predefined symmetry. Upon rapid cooling at 5 °C/min, the monomer also exhibits a metastable, monotropic ferroelectric smectic C* phase from approximately 35 to 33 °C. The cross-linking of this metastable phase will also be discussed.

*Keywords:* ferroelectric liquid crystals; cross-linked; smectic; diacrylates

## INTRODUCTION

Solid-state materials that are highly ordered and lack a center of symmetry exhibit a number of interesting phenomena[1-3]. For example, noncentrosymmetric ordered networks formed from the alignment and polymerization of LC diacrylates in the smectic C* phase exhibit piezoelectric and pyroelectric properties (Scheme 1).

SCHEME 1 Formation of a noncentrosymmetric polymer network.



The unique properties of LC monomers provide a high degree of order and processibility, and the presence of a chiral moiety removes the center of symmetry in the bulk assembly.

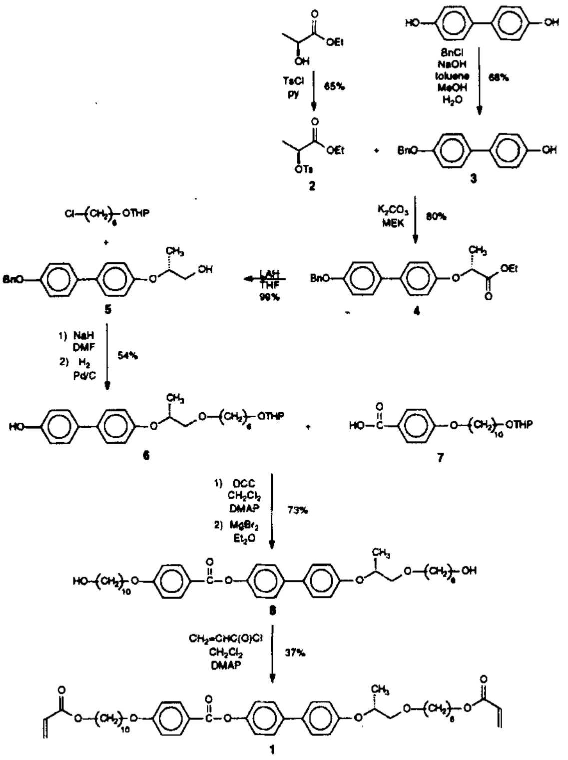
The preferred method of generating cross-linkable, chiral LC phases has been to add a nonreactive or monoacrylate chiral component to an LC diacrylate mixture[4-10]. The resulting polymer networks tend to lack thermal, mechanical, and temporal stability due to the chiral component retaining a high degree of mobility within the cross-linked network[7]. Intrinsically chiral LC diacrylates would generate ordered noncentrosymmetric networks with stable properties. These chiral LC diacrylates are rare because of the difficulties associated with the design of such monomers. Only one example of a chiral, smectic LC diacrylate has been reported and its synthesis is elaborate and requires enantiomeric resolution[10]. Herein we present the synthesis and subsequent photopolymerization of a new chiral smectic diacrylate **1** derived from (*S*)-ethyl lactate.

## EXPERIMENTAL SECTION

### Synthesis of the Diacrylate Monomer

The synthesis of the diacrylate monomer **1** is shown below (Scheme 2). The detailed synthesis is described previously in the literature[11]. (S)-Ethyl lactate is first reacted with p-toluenesulfonyl chloride to afford **2**. Monoprotected 4,4'-biphenol **3** is then added to tosylate **2** to yield ether **4**. Reduction of **4** with lithium aluminum hydride affords chiral platform **5**. THP-protected 6-chlorohexan-1-ol is then added to **5** and subsequent removal of the benzyl group affords the phenol **6**. Ethyl 4-hydroxybenzoate is reacted with THP-protected 10-chlorodecan-1-ol to yield **7**. Subsequent coupling of **6** and **7** using DCC affords the THP-protected form of the target monomer. Removal of the THP groups with magnesium bromide, followed by a diacrylation with acryloyl chloride yields the LC diacrylate **1**.

SCHEME 2 Synthesis of the monomer.



## Instrumentation

Low-angle X-ray diffraction profiles were taken on an Inel CPS 120 powder diffraction system employing Cu Kα radiation. This system was equipped with an Inel capillary oven for variable-temperature studies. Polarized-light microscopy (PLM) was conducted on a Leica DMRXP POL microscope with a Linkam THMSE 600 hot stage controlled by a Linkam TP 92 temperature controller. PLM photographs were obtained with a Wild MPS 48/52 automatic camera assembly. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC-7.

## Preparation of Photopolymerizable Monomer Mixtures

2,2-Dimethoxy-2-phenylacetophenone (2 wt %) was dissolved with monomer **1** in $CH_2Cl_2$. The solvent was subsequently removed in vacuo to afford the reactive monomer mixture.

### Photopolymerization of Monomer Mixtures in the Smectic A* and C* Phase

4 mg of the monomer mixture was placed between two KBr plates and heated to the isotropic melt using the microscope heating stage. The mixture was then cooled at 2 °C/min to 63.4 °C and then irradiated with 365 nm light (11,000 μW/cm$^2$) for 10 min with the sample temperature maintained by the heating stage. The sample resulted in the cross-linked network from the smectic A* phase.

For the network resulting from the smectic C* phase, the above procedure was followed except that the stage was cooled from the isotropic melt at 20 °C/min to a temperature of 33.0 °C and then photopolymerized for 10 min.

## RESULTS AND DISCUSSION

### Analysis of the Monomer

Before preparing the diacrylate for analysis, a nonpolymerizable analog was synthesized where terminal methyl groups were used instead of the terminal diacrylates. This molecule gave numerous mesophases upon heating and cooling and allowed us to proceed in confidence that the diacrylate would produce similar results.

The DSC thermogram of monomer **1** revealed two distinct thermal transitions at 49.2 °C and 71.0 °C upon heating at 0.5 °C/min and two transitions at 71.2 °C and 39.3 °C upon cooling at the same rate. Upon heating the crystalline sample above 49.2 °C, PLM revealed a focal conic fan texture characteristic of a smectic phase . The clearing point was observed at 71.2 °C from this smectic phase to the isotropic melt. When the sample was cooled back down from the isotropic phase, the same focal conic texture was seen by PLM and a polycrystalline texture was observed below 39.3 °C.

The broad smectic phase in this molecule was identified as a smectic A* phase. X-ray diffraction analysis of the sample at 50 °C revealed a single peak ($d_{100}$) at 44.3 Å. This layer spacing correlates very well with the calculated length of monomer **1** (44 Å)[12] and indicates that little to no tilt angle is observed in this mesophase. Further evidence for the smectic A* phase came from PLM where it was found that the sample could be homeotropically aligned between two glass plates. The sample did not respond to an applied electric field when homogeneously aligned in a rubbed ferroelectric LC cell. In addition, a Debye-Scherrer X-ray diffraction profile aligned in a strong magnetic field showed distinct organization characteristic of a smectic A phase.

Upon rapid cooling on the DSC (5 °C/min), an additional monotropic phase is observed from 36.5 °C to 23.9 °C. This metastable mesophase was determined to be smectic C* due to its focal conic texture and its ability to reorient when placed in an applied electric field.

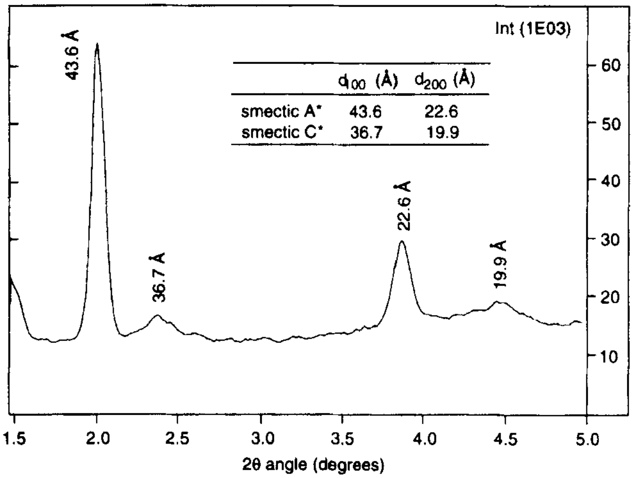
## Analysis of the Polymer

The monomer mixture (preparation described above) can be cross-linked in the smectic A* phase when heated to the appropriate temperature and then irradiated with 365 nm light (11,000 μW/cm$^2$). The extent of polymerization was followed by IR and was found to be ca. 80% after about 10 minutes.

This polymerized material exhibits nearly the same X-ray profile as the smectic A* monomer., indicating that the order of the smectic phase is locked-in upon cross-linking. The $d_{100}$ changed from 44.3 Å to 42.6 Å indicating a slight contraction of the matrix upon polymerization. The stability of this network is evidenced by the fact that the X-ray profile remained unchanged even after heating the network well above the clearing point of the monomer.

Due to its inherent instability, the monomer could not be polymerized entirely as the smectic C* phase. Attempts were made to attain such a network by cooling the monomer melt rapidly and then instantly photopolymerizing the phase; however, separated domains of cross-linked smectic A* and smectic C* regions resulted as seen by PLM and X-ray. The X-ray profile shows a new set of higher-angle reflections in addition to the smectic A* pattern seen before (Figure 1). These reflections correspond to the $d_{100}$ and $d_{200}$ spacings of a tilted smectic C* phase with a periodic layer spacing of 36.3 Å. Based on the calculated length of monomer **1**, this observed layer spacing is consistent with a tilt angle of 32.4 degrees.

FIGURE 1 Low-angle X-ray diffraction profile of monomer **1** containing cross-linked smectic A* and C* domains.



| | $d_{100}$ (Å) | $d_{200}$ (Å) |
|---|---|---|
| smectic A* | 43.6 | 22.6 |
| smectic C* | 36.7 | 19.9 |

## SUMMARY

A novel monomer has been synthesized that exhibits both a smectic A* and C* phase. Polymers formed from this monomer have been shown to retain the characteristics of the smectic A* or C* phase, depending on the temperature of polymerization. Structural modifications to monomer 1 are now being performed in order to create a more stable smectic C* phase.

### Acknowledgments

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[12] The extended length of **1** was calculated by molecular modeling using CS Chem3D Pro software, employing MM2 force field parameters.