Ferroelectric liquid crystals for second order nonlinear optics*

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Abstract: Main-chain ferroelectric liquid crystal polymers (FLCPs) and oligomers are of interest as precursors to free standing glassy fibers with the FLCP static structure. In particular, a supermolecular structure where the polar axis is oriented normal to the fiber axis may be of utility for frequency mixing applications. We report herein the synthesis of just such a main-chain FLCP wherein the disperse red NLO chromophore is oriented preferentially normal to the fiber axis. The new polymer has MW ≈ 40 000 by calibrated gel permeation chromatography, representing a degree of polymerisation of the 'side-by-side dimer' monomers of about 30 units. The phase sequence exhibited by this material (1–125°–SmC*–85°–glass) is useful for achieving the desired goal. Attempts to pull fibers from the SmC* phase were unsuccessful. But, nice free standing fibers were easily obtained from the isotropic melt by simple insertion and rapid removal of the closed end of a melting point capillary. Examination of 4 μm fibers by polarised light microscopy showed that the transition moment of the dye is preferentially oriented normal to the fiber axis, and that the fast axis of the birefringent fibers is along the fiber axis. These results suggest that the desired supermolecular structure has been achieved.

BACKGROUND

The FLC supermolecular structure

The chiral smectic ferroelectric liquid crystal (FLC) supermolecular structure is very appealing for nonlinear optics (NLO) applications [1]. This type of fluid ferroelectric combines the relative ease of processing inherent in liquid crystals with thermodynamically stable polar order. The basic structural features of chiral smectic FLCs are indicated in Fig. 1. Conventional calamitic liquid crystal molecules are composed of a rigid core and two 'floppy' tails, as indicated in the Figure by thick and thin lines, respectively. The molecules are organized in layers, with the director (n) tilted coherently off the layer normal (z) by the smectic C tilt angle. The plane containing the director and the layer normal is termed the tilt plane. When the molecules are enantiomerically enriched, this system, denoted SmC*, possesses only one two-fold symmetry axis and is therefore polar, with the polar axis along the two-fold axis, normal to the tilt plane. This polar symmetry allows the existence of a macroscopic electric dipole moment, the ferroelectric polarization. For most SmC* materials this polarization can be easily measured in electrooptic transparent capacitor cells in the surface stabilized FLC (SSFLC) geometry, where transparent conducting substrates are oriented parallel to the tilt plane, with the polarization normal to the substrates [2]. In addition, in samples where surface constraints allow it, the director precesses about

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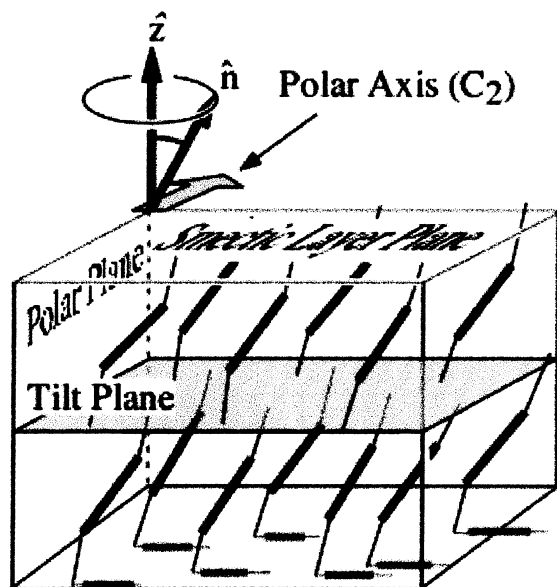
Fig. 1 Supermolecular structure of the chiral smectic FLC self assembly.

the tilt cone on passing from layer to layer, forming a helix whose axis is along the layer normal, and with a pitch typically on the order of 100–1000 times the molecular length.

In the context of the current discussion, it is critical to note that the polarization is normal to the average long axis of the molecules. This geometrical feature complicates the design of FLCs with large second order susceptibility $\chi^{(2)}$ along the polar axis. An approach to FLCs with useful $\chi^{(2)}$ has, however, been described [1].

Main-chain FLC polymers for NLO

Some attractive NLO applications involve optical wave mixing in polymer optical fibers. In this case it is useful to obtain fibers where the polar axis and the charge transfer axis of the NLO chromophore are oriented normal to the fiber axis. Rheological considerations suggested that a main-chain FLC polymer (FLCP) would afford this interesting supermolecular stereochemistry if the main-chain orients along the pulling direction during formation of the fiber, forcing the layers to form more or less normal to the fiber axis, the polarization being parallel to the layers. While side-chain FLCPs have been extensively studied [3], main-chain FLCPs have not, presumably due to a feeling among many workers in the field that such polymers would not show electrooptic switching in SSFLC cells. In fact, main-chain FLCPs can be quite well behaved, exhibiting nominal FLC switching in aligned transparent capacitor cells [4].

In initial studies aimed at obtaining main-chain FLCPs with useful $\chi^{(2)}$, acyclic diene metathesis polymerization (ADMET) of first-generation NLO FLC mesogenic dienes **2** was investigated as shown in Fig 2 [5]. Using the ruthenium alkylidene catalyst **1**, the polymerization was accomplished in the neat smectic LC phase of compounds **2**. The transformation produced smectic oligomers **3**, with degree of polymerization of about 10. As indicated in the Figure, the ADMET oligomers **3** have excellent mesogenicity; substantially better than that of the diene monomers. The glass transition temperatures, however, are below room temperature, and in our hands oligomers **3** did not provide stable free standing fibers upon pulling from the isotropic melt or from the LC phases. Perhaps more importantly, the NLO chromophore present in these oligomers (the o-nitroalkoxyphenyl unit), while well oriented along the polar axis, provides a small $\chi^{(2)}$, with a maximum d coefficient of about 0.6 pm/V for second harmonic generation from a 1064 nm fundamental [6].

Side-by-side dimer FLC NLO mesogens

As we have discussed in detail in the literature [1], the problem of enhancing $\chi^{(2)}$ in FLCs is complicated by the fact that chromophores possessing large molecular second order susceptibility β typically have
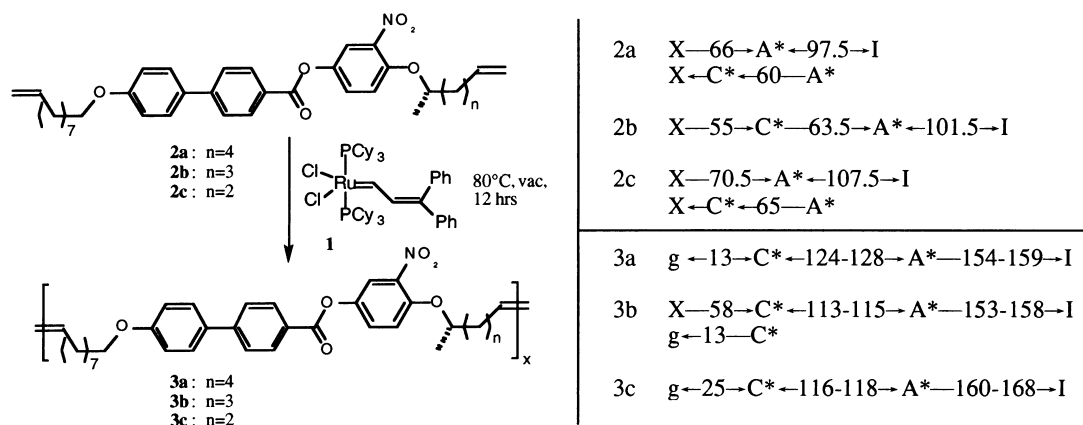
Fig. 2 Main-chain FLC oligomers by ADMET polymerization.

a large aspect ratio, with the charge transfer axis along the long axis of the molecules. This assures that in the FLC system, the charge transfer axis will orient parallel to the director, normal to the polar axis. This, of course, is incorrect stereochemistry for achieving large macroscopic $\chi^{(2)}$.

Our approach for improving this situation is illustrated in Fig. 3. In this case, two mesogens, one bearing an electron donor, and the other an acceptor, are linked in a 'side-by-side' manner to provide mesogens of type **4**. Compound **4** itself possesses a narrow enantiotropic SmA* phase.
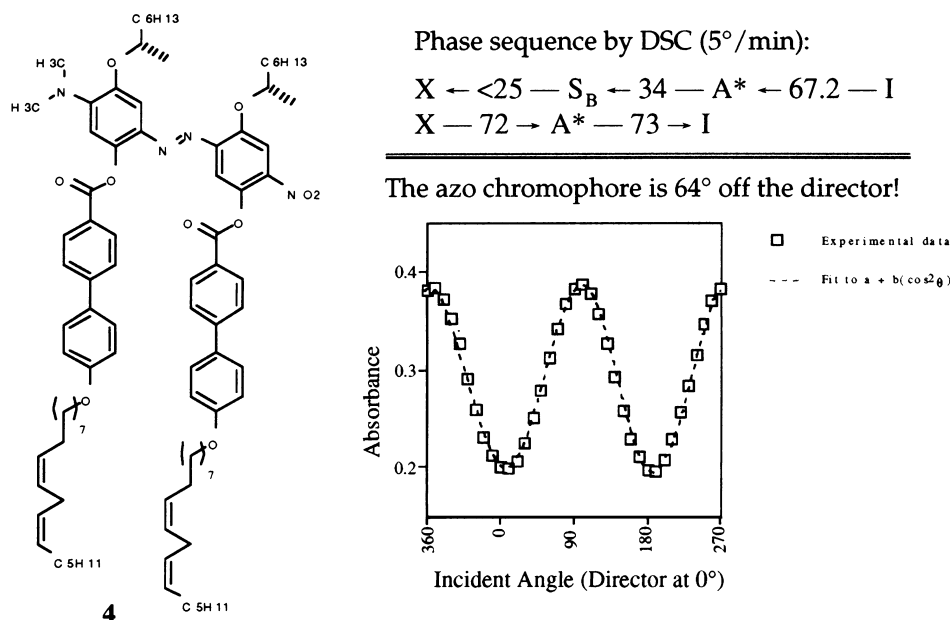

Fig. 3 Prototype 'side-by-side' NLO FLC mesogen.

Experimentally observed nonresonant linear optical properties and visible light dichroism in aligned samples of **4** establishes the basic structure of this SmA* phase. The fast axis of the system is along the layer normal of the SmA*, parallel to the director. Compounds of type **4** represent the only known SmA materials with this property (negative birefringence) outside of the thalium salts of some long chain carboxylic acids. Furthermore, the transition dipole for resonant absorption is preferentially oriented normal to the liquid crystal director (note maximum transmission when the plane of polarization of incident light at the absorption maximum of the chromophore (510 nm) is oriented parallel to the director). Finally, X-ray scattering data confirm the SmA* assignment. In addition, the observed layer

spacing of about 47 Å is equal to the molecular length of one of the mesogenic units in the dimer structure. All of these data taken together prove that the basic supermolecular stereochemistry required for enhanced $\chi^{(2)}$ FLCs can be achieved using the side-by-side dimer strategy.

MAIN-CHAIN POLYMERS FROM SIDE-BY-SIDE DIMERS

Synthesis and characterization of new main-chain FLCPs

These prior results suggested synthesis of a side-by-side dimer main-chain ADMET polymer as a promising approach for NLO FLCPs. To this end, the side-by-side dimer diene **5** was polymerized as indicated in Fig. 4. The dimer **5** is itself a mesogen showing a monotropic SmC* phase (phase sequence on heating: X–97–I; on cooling: I–88–SmC*–65–X). In this case, however, the high viscosity of FLC **5** precluded polymerization directly from the SmC* phase. As indicated in the Figure, ADMET polymerization was quite effectively accomplished using the commercially available ruthenium alkylidene catalyst **6** in dichloroethane solvent, providing the novel polymers **7**. This was gratifying given the highly functionalized nature of the diene **5**, and the fact that imines very effectively poison catalyst **6**. Apparently the catalyst is neither effected by azobenzene units, nor by dimethylaniline units. Shorter reaction times produced polymer of lower molecular weight, while longer times did not change the properties of the product.
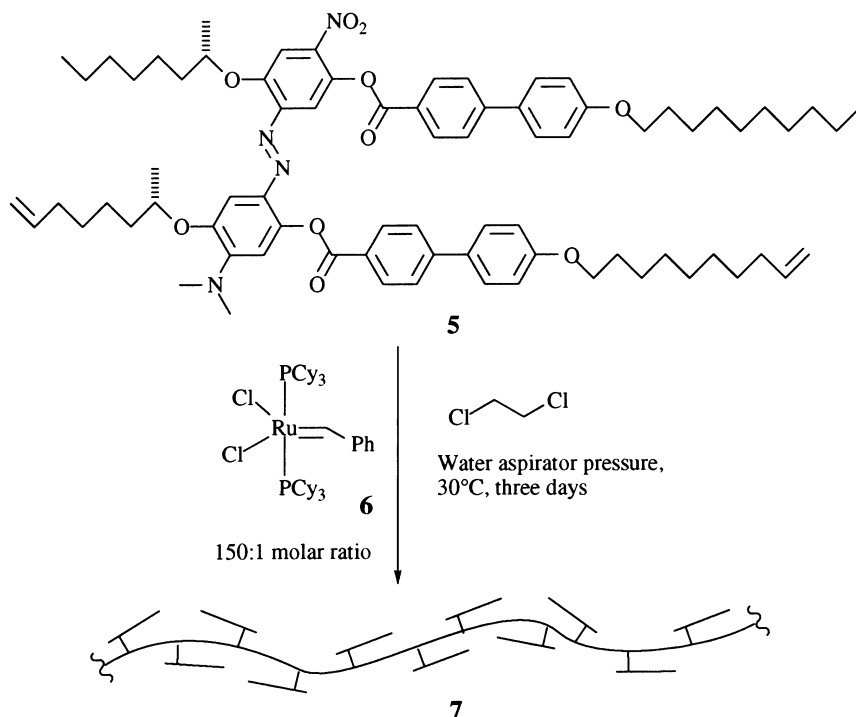

Fig. 4 Synthesis of main-chain polymers from side-by-side dimer dienes.

For oligomers **3**, the molecular weights could be easily estimated using end group analysis (integration of signals from the terminal alkene units) by ^{1}H NMR. In one polymerization run of diene **5** the catalyst was apparently poisoned, allowing isolation of a sample of dimer as evidenced by ^{1}H NMR end group analysis. While the terminal double bonds could be easily seen in this material, both ^{1}H and ^{13}C NMR analysis suggested that the dimer is a mixture of three constitutional isomers, as expected. This serves to point out explicitly that metathesis provides random head-to-head, head-to-tail, and tail-to-tail connections; there is no polar order along the main-chain in oligomers prepared in this way. Polymers **7** should thus be composed of a complex mixture of constitutional isomers with no polar order along the main-chain. For FLCs this is not directly relevant, since the polar axis is normal to the director/main-chain.

For polymer **7**, ^{1}H NMR failed to reveal the end groups, suggesting a higher molecular weight than had been obtained for polymerization of dienes **2** in the neat smectic phase. Consistent with this argument, gel permeation chromatography of polymer **7** indicated a hydrodynamic radius equal to that of a polystyrene standard of 40 kDaltons. A 40 k MW for polymer **7** represents a degree of polymerization of about 30.

As was found previously, the smectic mesogenicity of the material obtained by ADMET polymerization is improved relative to that of the starting diene. Analysis of the material by polarized light microscopy (PLM) in thin films indicated the enantiotropic phase sequence: I–125–SmC*–85–glass. In the SmC* phase the material showed typical electrooptic switching behavior. Unfortunately, the switching speed was so slow, apparently due to high viscosity, that a reliable estimate of the magnitude of the polarization could not be obtained. The sign of the polarization, however, was observed to be positive, in agreement with expectation for the indicated enantiomer of the chiral mesogen. The glass transition temperature was taken as the temperature at which electrooptic switching could no longer be observed. The optical texture of the glass was indistinguishable from that of the above-lying SmC* phase, again as expected. Differential scanning calorimetry (DSC) clearly showed the phase transitions, though no glass transition could be observed. DSC showed no signs of crystallization for polymer **7**.

Analysis of bulk, unaligned samples of the new materials by X-ray scattering was completely consistent with the phase identifications made by PLM. The only scattering peaks (aside from the usual diffuse scattering from the nearest-neighbor spacings) were due to the smectic layers. The experimentally measured layer spacings as a function of temperature for monomer **5**, dimer, and two samples of polymer **7**, are shown in Fig. 5. The layer spacings vary only slightly with temperature, as expected for a material with an I–SmC transition (such transitions are typically first order). Note that the layer spacing for dimer is smaller than that of diene monomer **5** by about 1.5 Å, and that the polymer **7** layers are smaller still. This is fully consistent with the shrinking 'mesogen length' of monomer, dimer, and large oligomers in this system deriving from the fact that a carbon is lost from the main-chain at each metathesis step. Rough analysis of the mesogen lengths using a fully extended MM2 minimum suggests that the X-ray tilt (defined as arccos (layer spacing/mesogen length) is approximately 40° for all of the measured materials. Again, such a large tilt angle is typical for I–SmC materials. Finally, no sign of crystallization could be observed in the polymer samples by X-ray scattering, even after several days at room temperature. It should be mentioned that the sample of polymer **7** labelled 'polymer 2' in Fig. 5, shown to have a slightly larger layer spacing than the sample labelled 'polymer 1', also showed a lower molecular weight by gel permeation chromatography. The hydrodynamic radius of this sample, prepared by ADMET for only two days, was equal to polystyrene of about 30 k MW, though no terminal double bonds could be observed by ^{1}H NMR.
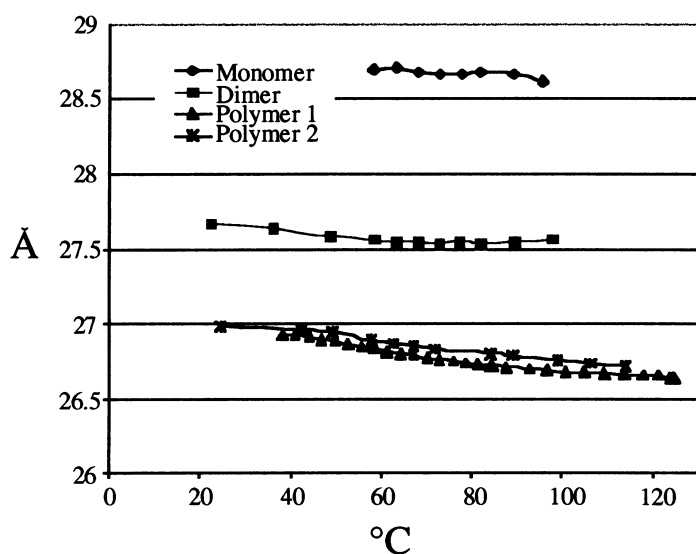

Fig. 5 Layer spacings determined by X-ray scattering as a function of temperature for the new materials.

The supermolecular structure of fibers pulled from polymer 7

Attempts to pull fibers from the SmC* phase of polymer **7** were unsuccessful. Nice free standing fibers could be easily obtained, however, by simply pulling from the isotropic melt. Thus, a sample of polymer **7** was put in a small cup and heated above the clearing temperature. A small capillary tube was then dipped into the melt and quickly removed. This provided very robust fibers with diameters of about 4 μm to 30 μm, depending primarily upon the pulling rate. These fibers showed good extinction by PLM when observed between crossed polarizer and analyzer with the fiber axis either parallel or perpendicular to the polarizer. Red transmitted light with a smooth texture was observed upon rotation of the fiber axis to 45° from the polarizer. This is consistent with good alignment in the fibers, with the director either parallel or perpendicular to the fiber axis.

Since the chromophore in polymer **7** should be anisotropically oriented in the fibers, they then should act as polarizers. Indeed, removal of the polarizer in the PLM system, such that only the fiber and analyzer were present, provided an indication of the orientation of the chromophore. Specifically, when thin fibers were observed with unpolarized input light, a maximum in transmission through the analyzer was seen when the analyzer was parallel to the fiber axis. Furthermore, it was shown that the fast axis in the fibers was also parallel to the fiber axis. All of these observations are consistent with a supermolecular structure in the fiber where the LC director and polymer main-chain are preferentially oriented along the fiber axis, and the smectic layers and the azo chromophore make a large angle with the fiber axis. Of course this also implies that the polar axis and NLO charge transfer axis are at a large angle to the fiber axis, as desired.

The observation that main-chain polymers **7** exhibit 'flow-aligning' behavior is particularly interesting. Rheological investigations of a main-chain liquid crystalline polyester with transitions from nematic to smectic, indicated that flow-aligning behavior occurred in the nematic phase, but non-flow-aligning behavior (i.e. tumbling) was seen close to the transition to the smectic phase [7]. This is likely due to the competition between the tendency of the main-chain to orient parallel to shear at odds with the tendency for the smectic layers to orient parallel to shear. This provides a good explanation for the lack of success in obtaining fibers when pulling directly from the SmC* phase of polymer **7**. More recently, Sierra *et al.* have demonstrated by X-ray diffraction studies on drawn fibers flow-alignment similar to that reported here (main-chain parallel to the fiber axis) in a main-chain SmC* polyester [8]. The details of the layer structure in fibers of polymer **7** are under investigation. One attractive possibility is that the chirality of the system is manifested in a novel type of SmC* helix where the director is along the fiber axis, and the layer normal precesses about the director. Such a helical structure cannot fill space without defects, and an especially interesting possibility is that the fiber is one giant screw dislocation, with a layer structure reminiscent of a spiral staircase and the polarization normal to the fiber axis. Such a structure should have a helical periodicity in the refractive index due to the biaxial nature of the SmC* phase, affording a photonic bandgap useful for enhancement of NLO effects in the fiber [9].

CONCLUSIONS

In conclusion, it has been demonstrated that broad temperature SmC* main-chain polymers with glass transitions well above room temperature are obtained by ADMET polymerization of highly functionalized side-by-side dimer FLC NLO mesogens possessing terminal double bonds. These polymers may be easily drawn into stable free standing fibers wherein the chromophore and the FLC polar axis are oriented at a large angle with respect to the fiber axis. This supermolecular stereochemistry, which would be difficult to achieve by other methods, is of potential utility in NLO applications.

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