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Communications to the Editor

Main-Chain Ferroelectric Liquid Crystal Oligomers by Acyclic Diene Metathesis Polymerization[1]

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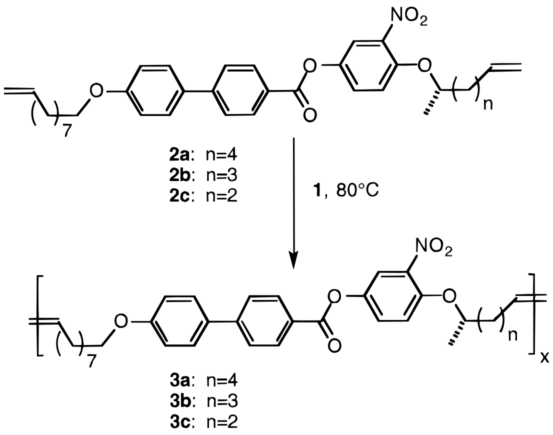
Ferroelectric liquid crystals (FLCs) are liquids with a thermodynamically stable polar supermolecular structure. This, combined with the excellent processibility of liquid crystals, makes FLCs an attractive approach for creation of organic second-order nonlinear optical (NLO) materials. Recently we have outlined an approach for obtaining a useful magnitude of the second-order NLO susceptibility in low molar mass FLCs.[1a−c,2] In addition, side chain FLC polymers (FLCPs) and oligomers can exhibit a structure similar to the low molar mass analogs, but with the processing advantages of LC polymers.[3] Herein we report the initial results of a program aimed at the preparation of main-chain FLC oligomers and polymers by acyclic diene metathesis (ADMET) polymerization.[4]

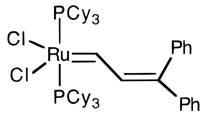
Until recently main chain FLCPs have been unknown, partly due to the perception that the tilted smectic structure and switching mode of FLCs are incompatible with main-chain LC polymer structure. Recent results, however, prove this perception incorrect. Indeed, main-chain FLCP siloxanes with excellent mesogenicity, high ferroelectric polarization, and nominal switching behavior in surface-stabilized FLC cells have been reported.[5] In the context of FLCs for NLO applications this is especially interesting, since it provides an approach for creation of free-standing fibers (main-chain FLCP glasses) with stable polar order where the polar axis is oriented normal to the fiber axis.[6]

Scheme 1. Synthesis of oligomers **3**



It has been suggested in the literature that siloxane end groups or spacer units segragate in such a way as to enhance smectic mesogenicity in FLC monomer and main-chain dimer structures.[7] We find, however, that this proposed effect is not necessary to obtain excellent smectic phase behavior in main-chain oligomers. Thus, a highly attractive approach for synthesis of main-chain FLCPs involves ADMET polymerization of a mesogen possessing vinyl groups at the ends of the tails. Since LC core units are typically rigid and rodlike, treatment of an "α,ω-diene" mesogen with a metathesis catalyst should lead to a main chain LC polymer with little competition from cyclization. Of course this approach requires a catalyst capable of sustaining metathesis in the presence of the functional groups found in the mesogenic diene. In particular, in order to apply the approach to our first-generation NLO FLC structures, the catalyst must be tolerant of aryl ether and nitro groups and the phenylbenzoate grouping.

We report herein that the ruthenium alkylidene complex **1**, recently shown to promote efficient cyclization of functionalized dienes,[8] also acts as an efficient catalyst for ADMET oligomerization of NLO FLC mesogenic dienes. The oligomerization takes place directly from the smectic A* liquid crystal phase of the monomer to the smectic C* phase of the oligomer (i.e. the sample is smectic liquid crystalline throughout the oligomerization reaction). Furthermore, the resulting oligomers possess excellent FLC properties in the context of FLCPs for NLO applications.



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Thus, as indicated in Scheme 1, when a neat mixture of a solid sample of one of the FLC mesogens **2** (LC phase sequences and transition temperatures of these diene mesogens are given in Table 1) and catalyst **1** (300/1 molar ratio) was heated to 80 °C under vacuum, bubbles of ethylene appeared immediately

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Table 1. Phase Sequence and Transition Temperatures of Diene Mesogens 2 and Oligomers 3

compd	phase sequence and transition temperatures
2a	X — 66 → A* ← 97.5 → I X ← C* ← 60 — A*
2b	X — 55 → C* — 63.5 ± A* ← 101.5 → I
2c	X — 70.5 → A* ← 107.5 → I X ← C* ← 65 — A*
3a	g ← 13 → C* ← 124–128 → A* — 154–159 → I
3b	X — 58 → C* ← 113–115 → A* — 153–158 → I g ← 13 — C*
3c	g ← 25 → C* ← 116–118 → A* — 160–168 → I

upon melting of the solid into the smectic A* phase. After 24 h under vacuum at 80 °C the mixtures (which seemed at this point to be liquid crystalline by direct observation) were allowed to cool to room temperature, and the resulting material was dissolved in 3 mL of benzene. Oligomeric products were obtained by precipitation from this benzene solution by the addition of 40 mL of a 0.5 M solution of HCl in methanol. A second precipitation from benzene followed by drying in vacuum gave oligomers **3** in ≅ 85% yield.[9] End group analysis by ^{1}H NMR suggested a degree of polymerization of about 10 (MW ~ 6 000) for oligomers prepared in this manner.

The LC phase sequence and transition temperatures for oligomers **3** are given in Table 1. Each sample was extremely viscous at room temperature, physically appearing to be a glass or microcrystalline solid. However, DSC measurements indicate that the actual glass transition temperatures for these oligomers occur below room temperature. For compound **3b** a peak corresponding to heat of fusion was observed by DSC at 58 °C on heating, showing that this materials is a supercooled crystalline solid a temperatures below about 60 °C. DSC analysis of samples of **3a**, however, never exhibited properties suggesting crystallization, even after many months at room temperature. In each case the "pure" material is smectic C* at 80 °C, with a very broad enantiotropic C* phase range.

In order to characterize the FLC properties of the materials, it was necessary to obtain good parallel-aligned samples between ITO-coated glass plates. While typical parallel alignment films such as rubbed polyimide or nylon failed to provide the required quality of alignment, a uniaxial Teflon monolayer[10] did in fact give well-aligned parallel samples. Using this technique for alignment, the ferroelectric polarization and smectic C* tilt angle as a function of temperature were measured for compound **3a**, as shown in Figure 1. As indicated in the figure, this material is a well-behaved FLC, exhibiting typical *P* and *θ* vs *T* behavior. Furthermore, the polar excess for the oligomer is high (≅ 40%) as evidenced by the observed large maximum ferroelectric polarization value of 639 nC/cm^2. This value is quite consistent with value observed for the low molar mass saturated analogue in this series (550 nC/cm^2), strongly suggesting that the polar structure in the oligomer is similar to that in the monomer. Since it is reasonable to assume that the $\chi^{(2)}$ of the oligomer is also similar to that observed for the analogous monomeric material, values of $d_{22} \sim d_{23} > 0.6$ pm/V for frequency doubling of 1064 nm light are expected for oligomer **3a** at temperatures below 70 °C.[2a] Experiments aimed at obtaining similar main-chain oligomers and polymers with higher glass transition temperatures are in progress.

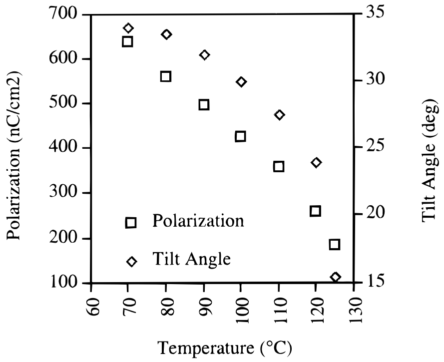

Figure 1. Experimental ferroelectric polarization and tilt angle as a function of temperature for a neat sample of oligomer **3a** (the sign of *P* is negative for all of the materials described herein). Below 70 °C the sample became so viscous that SSFLC switching was not fast enough to provide a good value for *P*.

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[9] Oligomers **3**, which are mixtures of constitutional isomers, showed ^{1}H NMR spectra fully consistent with the proposed structures and gave satisfactory combustion analytical data. While no direct information regarding the cis/trans double-bond ratio in oligomers **3** was obtained, catalyst **1** tends to give trans double bonds in methathesis products.

[10] Wittman, J. C.; Smith, P. *Nature* **1991**, *352*, 414–417.