Communications to the Editor

Synthesis of a Novel Dendritic Liquid Crystalline Polymer Showing a Ferroelectric SmC* Phase

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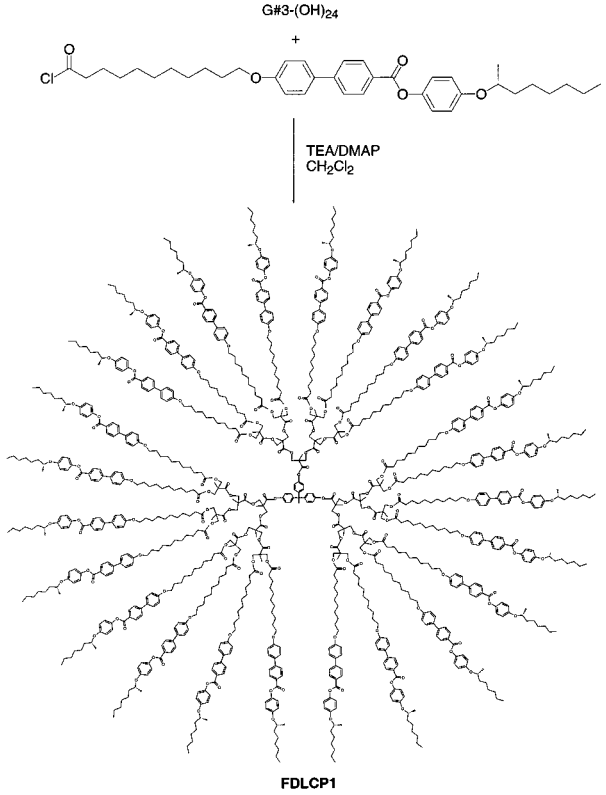
Generally, liquid crystalline polymers (LCPs) are divided into main-chain polymers, with mesogenic units that are coupled linearly, and side-chain polymers, with mesogens attached laterally to a flexible polymer chain.[1,2] A class of these LCPs are ferroelectric liquid crystalline polymers (FLCPs) where conventional mesogenic groups are replaced by chiral mesogens. Side-chain[3] and main-chain[4] FLCPs have been synthesized, and their physical properties have been investigated. FLCPs are regarded as interesting materials for optical switching and electrooptical applications, for example, in second-order nonlinear optics.[5] However, in contrast to low molecular weight ferroelectric liquid crystals (FLCs), their viscosity is often high due to chain entanglements. This leads to slow switching, which results in severe problems for practical application. Therefore, these limiting physical properties may be solved by using a novel type of polymeric structure.

In recent years, an innovative field of polymer chemistry has been the synthesis of dendrimers.[6,7] The most characteristic features of dendrimers in contrast to linear or branched polymers are the absence of entanglements and the low solution and bulk viscosities.[8] These macromolecules are distinguished by their three-dimensional fractal structure. Their synthesis requires monomers with an AB_m functionalization. Dendrimers can be constructed in successive synthetic steps, resulting in the formation of well-defined, unimolecular compounds. Many applications, including molecular encapsulation,[9] catalysis,[10] and polymerization initiators[11] have been developed for these highly branched macromolecules.

Recently, application of these dendritic molecules to the synthesis of LCPs has been emphasized. Percec et al.[12] reported on a dendrimer with mesogenic branching units, showing thermotropic nematic and smectic LC phases. A different approach has been the synthesis of liquid crystal functionalized dendrimers.

Scheme 1. Synthesis and Structure of FDLCP1



Lorenz et al.[13] reported on the synthesis of a functionalized dendritic carbosilane exhibiting a SmA phase. Previously, Ponomarenko et al.[14] described the functionalization of polyorganosiloxane dendrimers with different mesogenic groups, resulting in dendritic liquid crystalline polymers (DLCPs) showing SmA and SmC phases. Ferrocene-containing liquid crystalline dendrimers exhibiting a SmA phase have also been reported.[15]

In this paper, we present initial results of a study aimed at the synthesis and characterization of the first ferroelectric dendritic liquid crystalline polymer (FDLCP). In a recent paper, we underlined the double stage convergent approach for the synthesis of a hydroxyl functional dendritic aliphatic polyester.[16] In the present work, the third generation dendritic aliphatic polyester, bearing 24 hydroxyl groups on its surface, is functionalized with a ferroelectric mesogen. The mesogenic group, 4″-((*R*)-1-methylheptyloxy)phenyl 4-(4′-(10-(hydroxycarbonyl)decyloxy)-phenyl)benzoate, responsible for realization of the liquid crystalline state, is coupled to the dendritic matrix via acid chloride reaction (Scheme 1). The synthesis of the chiral mesogen will be reported elsewhere. The material is designated FDLCP1 in the further text. The purity of the final compound was established by ^{1}H NMR and size exclusion chromatography (SEC) measurements. For instance, the SEC trace of FDLCP1 consists of a

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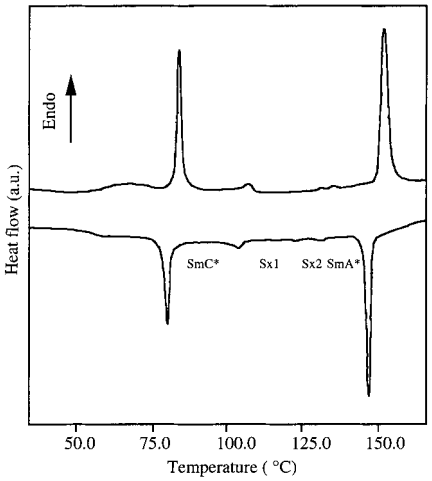

Figure 1. Thermograms of FDLCP1 upon heating (top curve) and cooling (bottom curve).

single peak after final purification and the compound shows monodispersity.[17]

Differential scanning calorimetry and optical polarized light microscopy studies of the mesogen reveal the presence of chiral SmA* and SmC* phases. The DSC thermograms of FDLCP1 are presented in Figure 1. The DSC data and the results obtained from optical polarized light microscopy investigations allow us to conclude that FDLCP1 exhibits a SmA* phase between 132 and 148 °C, and a SmC* between 80 and 105 °C. Both a focal-conic fan texture and a homeotropic texture are observed in the temperature range of the SmA* phase, whereas the SmC* phase displays typical Schlieren and broken focal-conic fan textures. The characterization of the two intermediate phases, Sx1 and Sx2, is still in progress, but their electrooptical behavior suggests that they are highly ordered phases.

FDLCP1 was introduced in a 4 μm shear cell of EHC type by capillary forces and electrooptical measurements were performed. The compound shows pronounced electroclinic effect in the SmA* phase.[18] By applying a DC electric field, it is possible to obtain an induced tilt angle. A typical plot of the induced tilt angle versus the applied electric field is shown in Figure 2. From the figure, it is clear that the induced tilt angle is a linear function of the applied voltage, even at rather high values of the tilt. The highest value is obtained at the limit of the SmA*−SmC* transition and is approximately 9° for a DC electric field of 20 V. Moreover, ferroelectric switching is observed in the Sx1, Sx2, and SmC* phases when applying a AC electric field. This result confirms that the Sx1 and Sx2 phases are tilted phases. Tilt angle measurements were performed in the Sx2, Sx1, and SmC* phases. As shown in Figure 3, a maximum value of 26° is obtained at 105 °C. The decrease of the tilt angle in the SmC* can be explained by the high viscosity of the material in this phase. Consequently, it is difficult to unwind the helix of the ferroelectric chiral SmC* phase unless a high DC electric field is applied.

In addition, when applying a DC electric field over the SmC* phase at 101 °C, it is possible to give a unique direction to the optic axis, tilted with respect to the smectic layer normal and thus resulting in the formation of a ferroelectric mono-domain between the electrodes. Surprisingly, no change in the texture of the film, i.e., no relaxation process, is observed when the electric field is turned off. Therefore, we suggest that a pyroelectric polymer is obtained where the macroscopically polar ferroelectric state of the SmC* phase stays locked.

(17) The SEC measurements for FDLCP1 gave M_w(calcd) = 16779 g/mol; M_w(SEC) = 14758 g/mol; M_n(SEC) = 14041 g/mol; PDI = 1.05.

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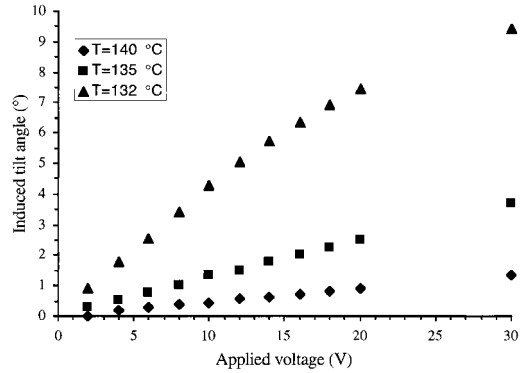

Figure 2. Induced tilt angle as a function of the applied voltage for FDLCP1 in the SmA* phase.

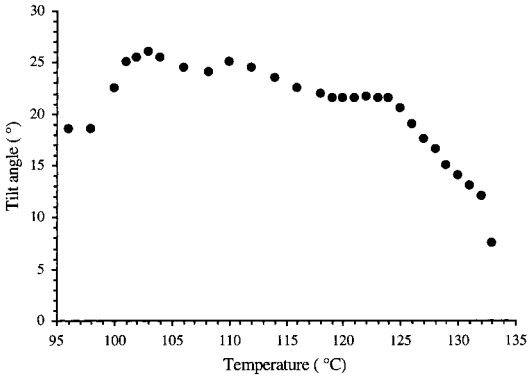

Figure 3. Tilt angle as a function of the temperature for FDLCP1.

Although there are many characterization aspects of this research which are requiring further investigations, we believe that the results reported in this paper have demonstrated both a new preparative and a new architecture interest for the field of FLCPs. The results have demonstrated the ability to synthesize a dendrimer which exhibits a ferroelectric smectic C* phase. We think this is a very rewarding result since it offers an alternative to side-chain and main-chain FLCPs. From a structural point of view, the formation of highly anisotropic SmA* and SmC* phases from a dendritic scaffold with radial symmetry functionalized with form-anisotropic mesogens appears to be contradictory. Therefore, this work opens new synthetic and theoretical opportunities in the areas of both ferroelectric liquid crystalline polymers and dendrimeric polymers research.

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