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Polymerizable Ester-Type Banana Liquid Crystals: A Comparative Study of Mesophase Behavior

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Summary: Two families of ester-type banana monomers are presented, 1,3-phenylene bis{4-[4'-(10-undecenyloxy)benzoyloxy]benzoate}s and 1,3-phenylene bis{[4'-(10-undecenyloxy)]-1,1'-biphenyl-4-carboxylate}s, in which the nature of the substituents on the central phenyl ring and the side arms was varied. The mesophase behavior of the monomers, including B_2 and B_7 phases, was correlated with their chemical structure and was compared with that of analogous azomethine-type banana mesogens. It is also shown that the banana monomers can be incorporated into new architectures of liquid crystal polymers.

Keywords: banana monomer; banana polymer; liquid crystal; mesophase; structure-property relationship

Introduction

Perhaps one of the most surprising results in soft matter in the last ten years was the discovery that banana-shaped molecules without chirality could assemble in layered chiral mesophases and, by symmetry, have a spontaneous polarization in the layer plane.[1] The phenomena of ferroelectricity and antiferroelectricity in general require broken mirror symmetry, which is commonly induced by chiral building blocks in chiral smectic mesophases.[2] By contrast, the mirror symmetry of smectic phases may be broken spontaneously when the molecules are not classically rods but banana-shaped.[1] Such materials, consisting of achiral molecules, can be packed in smectic chiral layers by different ways which in turn produces a diversity of mesophases, so-called B mesophases.[3] At present at least seven of such mesophases can be distinguished that are designated by the code letters B_1–B_7. Some of them exhibit unusual physical properties,[4-6] including electro-optic switching in the B_2, B_5, and B_7 phases.

Several classes of banana molecules have been synthesized in the last years, the vast majority being constituted by liquid crystals of the azomethine-type.[7] Only a few polymers containing banana units are known.[8-10] Nevertheless, polymers are expected to add much value to their

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low-molar-mass counterparts. In fact, polymers from banana monomers could combine the unique properties of polymers with those peculiar to banana molecules giving rise to chiral phases without the existence of chiral centers in the constituent molecules. Specifically, incorporation of banana molecules into polymers can result in self-assembled materials in which the molecular dipole correlations are maximized and lead to highly polar structures.

Therefore, the main goal of this work was to study the influence of chemical variations on the central ring, side arms and terminal chain segments on the mesophase behavior of two families of ester-type banana monomers (Figure 1). These monomers would be very versatile starting materials for inclusion into various novel architectures of liquid crystal polymers. We also compare them with closely related azomethine-type banana liquid crystals.

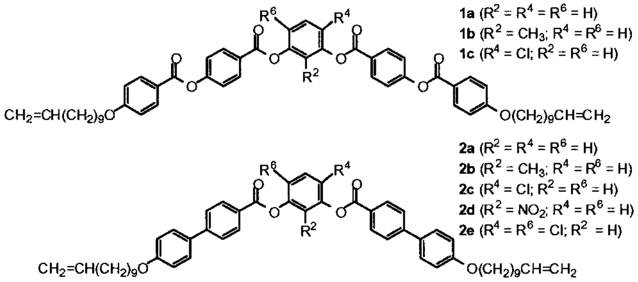

Figure 1. Chemical structure of the banana monomers investigated **1a-2e**.

Experimental Part

1,3-Phenylene bis{4-[4'-(10-undecenyloxy)benzoyloxy]benzoate}s[11] **1a-1c** and 1,3-phenylene bis{[4'-(10-undecenyloxy)]-1,1'-biphenyl-4-carboxylate}s[10] **2a-2e** were synthesized according to general literature procedures. Full details and characterization data will be given elsewhere.

Differential scanning calorimetry measurements were carried out with a Mettler DSC30 equipment with a 5 °C·min^{-1} scanning rate.

Mesophase structures were observed by Amplival Pol U polarizing microscope equipped with a Boetius hot stage.

The materials were filled in 4–10 μm thick cells purchased from Displaytech or EHC. The liquid crystal cells were placed in a computer controlled hot stage (STC200F from INSTEC) and the phase sequences were investigated by polarizing microscopy (BX60 from Olympus), electric current measurements and electro-optic studies. For these measurements Digital Oscilloscope (HP 54600B), Digital Multimeter (HP 34401A) and Arbitrary Waveform Generator (HP 33120A) were used.

Results and Discussion

Current understanding of the connections between the chemical structure of banana molecules and their mesophase behavior is limited and not comparable to that relatively well established for conventional rodlike mesogens. Most banana liquid crystals contain five phenyl rings, the overall bent shape deriving from a central 1,3-phenylene core.[7] Other structures of such liquid crystals have been produced by interconnecting varied numbers of different aromatic and heteroaromatic rings.[12-14] Starting from this general formula, different options for variation of the chemical structure may be considered.

We focused our attention on the nature of the substituents on the central phenyl ring and the side arms of purely ester-type banana mesogens (Figure 1). One special variation of the chemical structure is the use of alkenyl chains as terminal groups. The C=C double bonds of the vinyl groups, or those of other polymerizable moieties, in fact may be exploited to incorporate banana mesogens into new structures of polymers. The monomers **1a-c** and **2a-e** comprised a central 1,3-phenylene ring from resorcinol carrying substituent(s) of various nature (R^2, R^4, R^6= H, CH_3, Cl, NO_2) at different sites (2-, 4-, 6-positions). An undecenyl segment at both arm sides was the terminal tail in any case.

The phase transitions of the monomers greatly depended on their chemical structure (Table 1). In fact, there was a (monotropic) B_2 phase in **1a**, no mesophase in **1b**, and (monotropic) SmC and nematic phases in **1c**. The latter dimorphism is characteristic of calamitic liquid crystals. Introduction of a large chlorine substituent at the 4-position widens the bend angle of the non-substituted 1,3-phenylene ring (120°) to ~135°, rendering the molecules less prone to polar packing in layers.[7] This ability is more depressed in 4,6-dichlorosubstituted molecules, in which the bend angle is further enlarged to ~165° resulting in rodlike overall conformation, more typical of calamitic liquid crystals.[3] Consistent with this interpretation, **2e** only formed a (monotropic) nematic phase.

Table 1. Mesophase behavior of the banana monomers investigated.

Monomer	R^2	R^4	R^6	Phase transitions (in °C) [a)]
1a	H	H	H	Cr 101 (B_2 98) I
1b	CH_3	H	H	Cr 112 I
1c	H	Cl	H	Cr 74 (SmC 44) N 81 I
2a	H	H	H	Cr 138 I
2b	CH_3	H	H	Cr 137 I
2c	H	Cl	H	Cr 90 (N 82) I
2d	NO_2	H	H	Cr 110 B_7 118 I
2e	H	Cl	Cl	Cr 79 N 103 I

[a)] Cr: crystal; N: nematic; SmC: smectic C; B_x: different B mesophases, I: isotropic (monotropic phases in parentheses). By DSC and optical microscopy.

The B_2 phase, such as that of **1a**, is the most investigated B phase because of its different electro-optic responses.[15,16] It is a tilted polar SmCP phase with monoclinic chiral symmetry C_2. Depending on the relative orientations of the two-fold symmetry axis and the tilt direction, the layers can be right- or left-handed. In the adjacent layers the sign of the chirality can alternate or can be the same over micrometer ranges. Accordingly, two types of domains are possible: *racemic,* if the chirality in the adjacent layers alternates, and *chiral,* if the adjacent layers have the same handedness. The antiferroelectric (AF*)* racemic phase is synclinic, i.e. the molecules tilt in the same direction, and the textures usually have a high birefringence. In the chiral domains the AF state is anticlinic, i.e. the molecules tilt in opposite directions, and the birefringence is small.[17]

On cooling from the isotropic phase, **1a** presented textures with a weak golden birefringence indicating that the optical axis was parallel to the smectic layer normal (see the fan-shaped domains with horizontal and vertical Maltese crosses in Figure 2a). By applying an electric field ($E > 10\ V\cdot\mu m^{-1}$), the texture transformed to a state with a reddish birefringence color and simultaneously the Maltese crosses rotated by 45° indicating a director tilt $\theta = 45°$ (Figure 2b). This behavior may be attributed to a structure where the molecular plane is parallel to the film surfaces and the smectic layers are tilted by an angle equal to the director tilt angle θ.[11] Such virgin structures were observed previously for synclinic antiferroelectric and synclinic ferroelectric states.[4]

It was surprising that neither **2a** nor **2b** showed any mesophase. This finding is at variance with frequent observations that small groups at the 2-position are normally beneficial to the onset of B phases. We attribute this suppression of mesophase behavior to the presence of shorter and stiffer biphenyl arms with respect to bisbenzoate arms of **1a** and **1b**. On the other hand, the electronic distribution throughout the molecule could be modified negatively and, in consequence, their capability to pack in layers would be reduced.[18]

Figure 2. Textures of **1a** at 80 °C in 4 μm cells: Virgin texture on cooling from the isotropic phase with no field (left); Texture transformed by E = 10 V·μm^{-1} field (right).[11]

Monomer **2d** presented a helical superstructure on cooling from isotropic melt, which is characteristic to B_7 textures.[19] By applying an electric field during the phase transition the smectic front showed a jerky motion with the frequency of the applied field (Figure 3). This is reminiscent of the behavior of some B_7 materials, which were identified as smectic with triclinic symmetry.[20] The sample presented an electro-optic switching between 112 °C and 118 °C. Below this temperature range, no electro-optic switching was detected, but there was a clear ferroelectric-type polarization peak that disappeared in the isotropic phase and decreased slowly toward lower temperatures. The helical superstructure is probably connected to the layer chirality, which arises from the simultaneous director tilt and polar ordering.[19] Since the constituent molecules contain no chiral center, this situation is different from the cholesteric or smectic C* phases, in which the molecular chirality leads to spiraling of the mean orientation of the molecules with respect to the helix axis.

Several families of azomethine-type banana mesogens, such as **3a-e** (Table 2), are known as opposed to the present ester-type systems. The data in Table 2 are compiled by selecting closely related mesogens from literature that contain the same n-dodecyl terminal chain. The trends of the B mesophase–isotropic phase transition temperature with chemical structure may be different in these series and establishing general guidelines for the preparation of materials with controlled phases and properties is still a challenge.

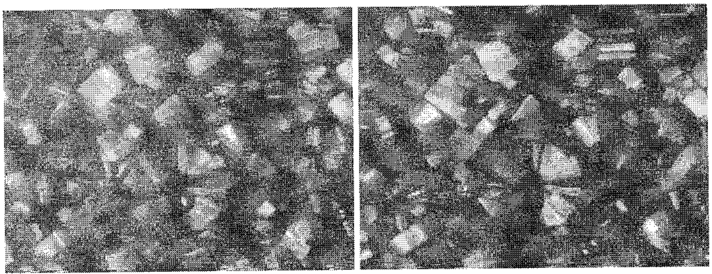

Figure 3. Textures of **2d** at 110 °C in 8 μm cells under ± 15 V·μm^{-1} fields.

We believe that the very peripheral double bond in the undecenyl terminal chain of **1a-2e** should not exert a significant influence on their mesophase behavior, which is therefore qualitatively comparable to that of mesogens **3a-3e**. Evidently, the azomethine homologues present a stronger tendency to mesomorphism, especially including the occurrence of B phases in various sequences. However, they have high melting temperatures, in the proximity of 100 °C, whereas the ester homologues generally present lower melting temperatures and mesophase ranges closer to ambient.

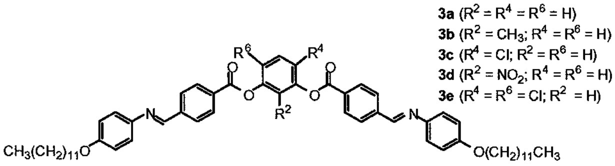

Table 2. Mesophase behavior of banana mesogens of the azomethine-type **3a-3e**.

Monomer	R^2	R^4	R^6	Phase transitions (in °C) a)
3a[21]	H	H	H	B_4 139 B_3 152 B_2 174 I
3b[22]	CH_3	H	H	Cr 148 B_2 164 I
3c[23]	H	Cl	H	Cr 115 B_2 142 I
3d[19]	NO_2	H	H	Cr 85 B_7 173 I
3e[24]	H	Cl	Cl	Cr 111 SmC 113 SmA 121 N 137 I

a) Cr: crystal; N: nematic; SmC: smectic C; SmA: smectic A; B_x: different B mesophases, I: isotropic.

The influence of the connecting groups between the phenyl rings on the mesophase behavior of banana liquid crystals appears unusually strong with respect to rodlike mesogens and must affect considerably the special packing of the bent molecules within the layers.

While banana mesogens **1** and **2** deserve attention in their own right, they should also serve as monomers to be introduced into new polymers with controlled macromolecular architecture. As one example, we have incorporated monomer **2e** along with a diacrylate monomer **4** into a main chain polymer poly(**2e**-*alt*-**4**) via acyclic diene metathesis polymerization[10] (Figure 4).

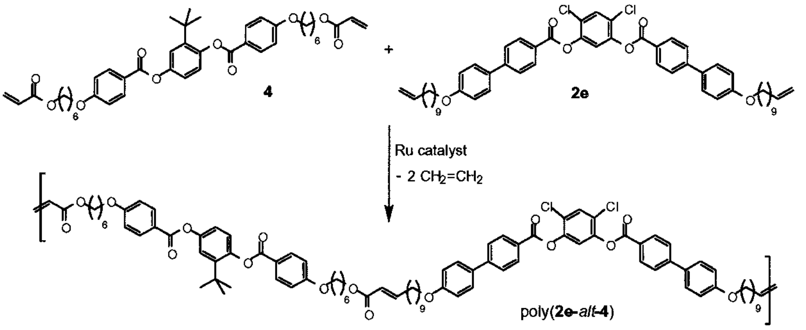

Figure 4. Reaction scheme for the preparation of an ALTMET polymer from banana monomer **2e** and diacrylate **4**.[10]

Treatment of 1:1 mixtures of monomers A (diene) and B (diacrylate) in the presence of $RuCl_2(=CHPh)(PCy_3)$(*N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-yl) yielded the corresponding alternating copolymers poly(A–B) in high yields, with elimination of ethylene. Such alternating metathesis polycondensation, that was named ALTMET, probably proceeds by first polymerization of the diene A followed by incorporation of the diacrylate B in a strictly alternating fashion.[10] Poly(**2e**-*alt*-**4**) gave rise to a nematic phase between the T_g at 46 °C and the T_i at 118 °C. Therefore, creation of well-defined and controlled polymers can enlarge the scope for studies of novel banana monomers with optimized chemical structures.

Conclusions

The ester-type banana-shaped monomers investigated present a variety of mesophases but, in general, seem to be less prone than azomethine-type liquid crystals to give rise to B mesophases. They can be incorporated into new polymer architectures. The most prominent physical properties of these materials in photonic applications can be ferroelectricity-antiferroelectricity for electro-optics of polymer gels and second harmonic generation in non-linear optics of polymer networks.

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