



Helical Super-structure from Achiral Liquid Crystals

Abstract

The objective of this research is to study the origin of chirality and helicity with the asymmetric, achiral biphenyl derivatives (BMC6, BMMEC6, BMEC6, BMNC6 and BMPC6) containing different functions at different positions without the Schiff base groups. In this study, the combined techniques of differential scanning calorimetry (DSC), polarized light optical microscope (PLM) and wide-angle X-ray diffraction (WAXD) were used to study the morphology and structures of these new asymmetric biphenyl derivatives molecules.

Introduction

Formation of thermotropic liquid crystals relies on mesogenic groups having either rod-like or disc-shape. The basic molecular structures can be further modified in different aspects giving rise to controlled structural features of the mesophases.¹ In the past decade, one of the most interesting design of molecular architectures in liquid crystals is banana-shaped molecules (so-called bow-shaped) with a bend core in the center of the mesogenic unit. The phase structure formed in this type of molecules is not miscible with smectic phases of calamitic compounds.¹ Therefore, a series of separate phase nomenclature (B1 - B7 phases) has been identified.² Moreover, hockey stick-shaped molecules and twin molecules with bent molecular structures have also been introduced.² However, these systems do not follow the usual patterns of symmetric bananas with the rigid angular location in the center of the molecule.

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Since Meyer first reported the ferroelectricity of chiral liquid crystals due to a spontaneous macroscopic electric polarization derived from the polar order in a tilted, layered liquid crystalline phase, a lot of research has been carried because of its potential in several applications and scientific interests.¹ Although the ferroelectricity in liquid crystals without molecular chirality was already predicted by theory,¹ ferroelectric properties had been only found in SmC* phases of chiral molecules before Niori, et. al.² reported on antiferroelectricity in 1996 in a smectic phase formed by banana-shaped Schiff-base derivatives, first synthesized by Matsunaga, et. al. Another fascinating result from the achiral bent molecules is helicity.³ The chirality from the polar order in combination with the tilt of the molecules may be the reason for the formation of a helical domain in the B2 (antiferroelectric switchable phase), the B4 (blue phase), and the B7 (helical superstructure formation) phases.¹ Recently, Watanabe, et. al.⁴ summarized three possible models for the origin of chirality in such banana-shaped molecules: the tilting of molecules in smectic layers, the twist conformation, the twisting of the director to escape from the spontaneous polarization.

Experimental

Materials and samples

A hockey stick-shaped LC molecule 4'-[6-(3'-hydroxyphenoxy)-hexyloxy]-4-biphenylcarboxylic acid (BMC6) was synthesized in Dr. Harris's group by the four step substitution reaction. In addition, other two hockey stick-shaped molecules, 4'-[6-(3'-methoxyphenoxy)-hexyloxy]-4-biphenylcarboxylic acid (BMMEC6) and 4'-[6-(3'-hydroxyphenoxy)-hexyloxy]-4-biphenylcarboxylic acid ethyl ester (BMEC6), were also prepared by similar methods. In order to study the role of a bend at the phenyl ring for helical superstructure formation, linear-shaped molecules 4'-[6-(4'-hydroxyphenoxy)-hexyloxy]-4-biphenylcarboxylic acid (BMPC6) and 4'-[6-(phenoxy)-hexyloxy]-4-biphenylcarboxylic acid (BMNC6) were also synthesized. All final compounds were purified by column chromatography, followed by repeated crystallization, and their purity was confirmed using ¹H-NMR and thin-layer chromatography. The detailed synthetic procedures can be made available.

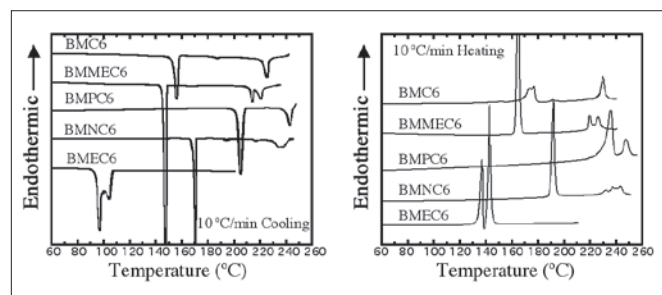


Figure 1. Set of DSC cooling and subsequent heating curves for four biphenyl derivatives at -10 °C/min.

Equipment and experiments

DSC was performed by a PerkinElmer® Diamond® DSC with an Intracooler 2P cooling apparatus. The temperature and heat flows were calibrated using standard materials at cooling rates ranging from 2.5 °C/min to 40 °C/min. When the cooling and heating rates were high, the sample weights were decreased correspondingly in order to avoid thermal gradients within the samples. Powder samples were used in differential scanning calorimetry (DSC) experiments. WAXD experiments were conducted with a Rigaku® 12 kW rotating-anode generator (Cu K α) coupled with a diffractometer. Phase morphology was examined via a polarized light optical microscope (PLM) (Olympus® BH-2) coupled with a Mettler® hot stage (FP-90). The textures were studied in sandwich-type cells with and without surface alignment layers or rubbing. The heating and cooling rates were 5 °C/min.

Results and discussion

Thermodynamic properties of phase transitions.

The transition temperatures and the enthalpy changes of biphenyl derivatives depend on their different functions and their positions, of which the -OH or -OCH₃ functions are at the para or meta positions on the phenyl ring and the -COOH or -COOC₂H₅ functions are at the para position on the biphenyl ring. The transition sequences with the cooling and heating rate of 10 °C/min are represented in Figure 1.

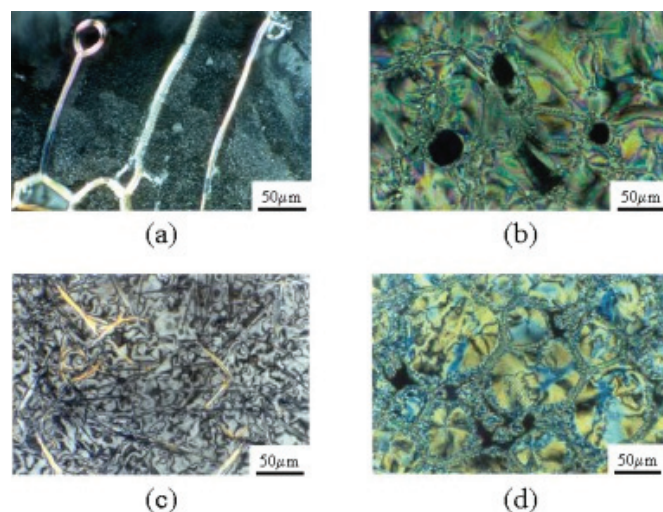


Figure 2. PLM morphological observations of four biphenylcarboxylic acid derivatives within an uncoated and unrubbed sandwich-type cell: (a) a S2 phase of BMC6 at 223 °C during cooling (-5 °C/min) from the S1 phase; (b) a S2 phase of BMMEC6 at 218 °C during heating (5 °C/min) from the S3 phase after cooling (-5 °C/min) from the isotropic phase; (c) a S3 phase of BMPC6 at 218 °C during cooling (-5 °C/min) from the S2/S1 phase; (d) a S2/S3 phase of BMNC6 at 231 °C during cooling (-5 °C/min) from the S1 phase.

On exchanging the -OH of phenyl ring in BMC6 to -OCH₃ at the meta position in BMMEC6, the transition temperature of Iso-to-S1 decreased about 2 °C from 219 °C (BMC6) to 217 °C (BMMEC6), the S2-to-S3 transition decreased about 18 °C from 191 °C (BMC6) to 173 °C (BMMEC6), and the S3-to-X transition decreased about 8 °C from 159 °C (BMC6) to 151 °C (BMMEC6). This could be due to the decrease of inter-layer interaction that may come from the hydrogen bond between phenol functions in BMC6. On the other hand, when the -OH function at the meta position in BMC6 is relocated to the para position in BMPC6, all the transition temperatures increased about 18 °C at the Iso-to-S1/S2 transition, 36 °C at the S1/S2-to-S3 transition, and 50 °C at the S3-to-X transition. This can be explained by the fact that the intermolecular hydrogen bond between the phenol functions of BMPC6 in the interlayer is stronger than that of BMC6 because of steric reasons. The enthalpy changes at the Iso-to-S1 transition in the 4-biphenylcarboxylic acid derivatives are higher than the normal enthalpy change in the Iso-to-LC phase transitions. This can be from the intermolecular hydrogen bonded self-assembly between the two carboxylic acids, which forms a dimer. This estimation can also be confirmed not only by the smectic layer thickness measurement using the WAXD powder pattern, but also by the fact that BMEC6 has no stable mesophase and cannot form the dimer by hydrogen bonding. In BMC6, BMMEC6, BMNC6 and BMPC6, the higher temperature transitions do not depend on the cooling and heating rate. However, the lowest temperature transition depends on the cooling rate. Different samples of BMEC6 show different numbers and shapes of exothermic peaks even though the cooling rate is same. This may be due to the vagaries phenomena during the crystallization of BMEC6.

Phase structural identifications

The PLM morphological observations of four biphenylcarboxylic acid derivatives within an uncoated and unrubbed sandwich-type cell are represented in Figure 2. In the case of BMC6, on cooling from the isotropic phase to the S1 phase at 5 °C/min, many small birefringent droplet rings having maltese crosses are at first formed just below the clearing temperature but the background is black. These small droplets start to merge together and make bigger droplets, but some of them break and make two lines. These two lines then start to grow along the thread long axis at the same speed but the width of thread does not change although the threads can laterally combined with others. Finally, when it is cooled down to 228 °C, an oily streaky texture (Myelin-figure) with equal widths forms but the

background is still black like the B7 phase in nitro-substituted banana-shaped molecules¹¹ and the SmA phase in a lyotropic LC molecule.¹⁷ This phase is fairly stable at this temperature, which means the Myelin texture does not change much in the isothermal state down to 218 °C. On cooling below the S1-to-S2 transition (a broad transition exothermic peak with less than 1 kJ/mol) at 5 °C/min, the thread in the Myelin-figure starts to twist step by step or smoothly along the thread and then changes to the helical thread that is observed in the B7 phase of the nitro-substituted banana-shaped molecules.¹ It is important to remember that there is no strong bend at the center of the BMC6 dimer unlike conventional banana-shaped molecules (about 110-140° bending angle).¹

To investigate the roles of possible hydrogen bonding between the dimer layers, the bend in the phenyl ring and the formation of dimer due to the intermolecular H-bonding between carboxylic acids, four more molecules (BMMEC6, BMPC6 BMNC6 and BMEC6) are studied in addition. Very strikingly, all biphenyl carboxylic acid derivatives showed helical textures except BMEC6, which cannot form dimer.

Conclusion

Achiral bent (hockey stick-shaped) molecules (BMC6 and BMMEC6), achiral linear molecule (BMPC6 and BMNC6), and BMEC6, which cannot form a stable dimer by H-bonding between carboxylic acids were synthesized by a four step substitution reaction. The formation of the dimer in our system is important to form a helical thread in PLM but the functions (-OH or -OCH₃) at the *meta*- or *para*-position of the phenyl ring are not necessary. The chirality and helical texture seems to come from not only the specific packing of dimers but also the twist conformation of the individual dimers.

Acknowledgements

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References

1. Pelzl, G.; et. al. *Adv. Mater.* **1999**, *11*, 707.
2. Niori, T.; et. al. *J. Mater. Chem.* **1996**, *6*, 1231.
3. Link, D.R.; et. al. *Science* **1997**, *278*, 1924.
4. Thisayukta, J.; et. al. *J. Am. Chem. Soc.* **2002**, *124*, 3354.

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