

Synthesis and characterization of Reactive Banana-Shaped Mesogens

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Abstract

The synthesis of ester type, banana-shaped, photo – crosslinkable mesogens is described. The reactive mesogens, derivatives of 1,3-phenylene bis{4-[4'-(alken-1-yloxy)-biphenyl-4-carboxylate]benzoate}s, were synthesized varying the length of alkyl end groups. The obtained monomers and polymers were characterized by FT/IR, NMR spectroscopy, DSC, polarized optical microscopy, and X-ray diffractometry.

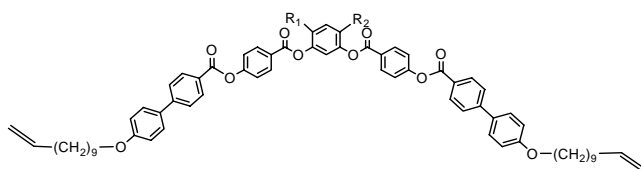
1. Introduction

Reactive mesogens are liquid crystalline materials that can be permanently fixed the liquid crystal phase by polymerization. The most common method to cross linking mesogens is UV photopolymerization. Therefore, the LC phase is locked into a thin, durable and plastic film that can be used as an optical element in various applications. Typical reactive mesogenic materials have the same core groups as electro-optic LC materials but with additional reactive groups to allow polymerization. monoacrylate or diacrylate reactive groups are used. Recently, rod-like type of reactive mesogens containing photocrosslinkable diene end groups have been reported.[1]

More recently, banana-shaped compounds have evolved as a new sub-field of liquid crystals, much effort has been devoted to the synthesis and physical characterization, especially after it was shown that they formed polar smectic phases, and that their polarization could be switched by electric fields.[2][3] The aim of this work is the investigation of the effect of rigidity and/or flexibility of the arms of banana shaped monomers with seven aromatic rings, where the terminal chains with polymerizable double bonds exist at both end of the molecule.

We report the first of synthesis reactive banana-shaped mesogens, a new class of banana monomers, 1,3-phenylene bis{4-[4'-(alken-1-yloxy)-biphenyl-4-carboxylate]benzoate}s PR1-PR3 and their UV photopolymerization.[Fig 1.]

In this work, we have investigated new banana-shaped mesogens composed of seven phenyl rings connected by ester linking group. We may developed that the novel reactive banana-shaped mesogens to be photopolymerized. Biphenyl was chosen as the part of the mesogen due to its tendency to form highly ordered smectic mesophases (often highly ordered smectic phases like S_E), and its lower crystal to smectic transition temperatures so that bulk polymerization can be easily controlled.



4a [$R_1 = R_2 = H$]

4b [$R_1 = Cl; R_2 = H$]

4c [$R_1 = R_2 = Cl$]

Figure 1. General chemical structure of the reactive mesogens.

2. Experimental

Synthesis.

The starting materials, 4'-hydroxy-4-biphenylcarboxylic acid, 4-benzyloxybenzoic acid, resorcinol, 4-chloro-resorcinol, 4,6-dichloro resorcinol, 11-bromo-undecene were purchased from Aldrich co., and used without further purification. Synthetic route is shown in Scheme 1.

1,3-Phenylene bis(4-benzyloxybenzoate) (1).

Reaction of resorcinol and 4-(benzyloxy) benzoyl chloride in presence of triethylamine were reacted for two days at room temperature, and then washed with water and dried over anhydrous sodium sulfate. The crude residue obtained after removal of the solvent purified by chromatography on silica gel using chloroform as an eluent. Removal of solvent from the eluate afforded a white product which was recrystallized from 1,4-dioxane. 1H NMR ($CDCl_3$, 400MHz) δ (ppm): 8.15 (d, 4H), 7.48-7.34 (m, 10H), 7.15-7.12 (m, 4H), 7.06 (d, 4H), 5.16 (s, 4H).

1,3-Phenylene bis(4-hydroxybenzoate) (2). The compounds was obtained by hydrogenation of (1) with 5% Pd/C catalyst in 1,4-dioxane. The residue was passed through a column of silica gel and eluted with a mixture of 4% acetone in chloroform. Removal of solvent gave a white product, which was recrystallized from ethyl acetate. 1H NMR (acetone- d_6 , 400MHz) δ (ppm): 9.7 (s, 2H), 8.06 (d, 4H), 7.54 (t, 1H), 7.22-7.2 (m, 3H), 7.0 (d, 4H)

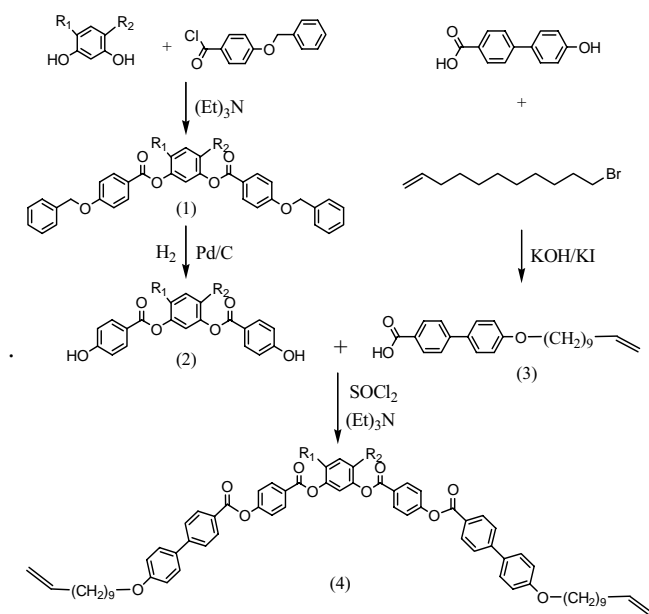
4'-(Undec-10-enyloxy)biphenyl-4-carboxylic acid (3).

The hydroxy-acid was dissolved in hot ethanol and water together with potassium hydroxide and a few crystals of potassium iodide. Undec-10-enyl bromide was added and the mixture was refluxed for 24hr. To hydrolyse any ester formed, a 10% solution of potassium hydroxide in 70% ethanol was added and refluxing was continued for an additional 3hr. The reaction mixture was allowed to cool and was acidified with concentrated hydrochloric acid. The solid formed was recrystallized from acetic acid and ethanol.

1H NMR (DMSO, 400MHz) δ (ppm): 7.98 (d, 1H), 7.75 (d, 2H), 7.67 (d, 2H), 7.03 (d, 2H), 5.79 (m, 1H), 4.96 (m, 2H), 4.00 (t, 2H), 2.00 (q, 2H), 1.73 (quintet, 2H), 1.2-1.5 (m, 12H)

4'-(Undec-10-enyloxy)biphenyl-4-carbonyl chloride.

Compound (3) and thionyl chloride were refluxed for four hours. The excess of the reagent was distilled off under the reduced pressure.



Scheme 1. Synthetic route to reactive mesogens.

1,3-Phenylene bis{4-[4'-(alken-1-yloxy)-biphenyl-4-carboxylate]benzoate}s (4).

1,3-Phenylene bis(4-hydroxybenzoate)(2) was reacted with 4'-(undec-10-enyloxy) biphenyl-4-carboxyl chloride in anhydrous 2-butanone in the presence of triethylamine for two days at room temperature. After reaction, the reaction mixture was poured into water. Then, the separated organic layer was washed with water until it became neutral, dried over magnesium sulfate and evaporated to dryness under vacuum. The reaction was monitored by TLC on Kieselgel 60 F254 sheet, and the spots were highly fluorescent under 254 and 366nm. The crude product was purified by flash chromatography on Kieselgel 60 (0.063 ~ 0.02 mm) column with 1,2-dichloroethane elution.

^1H NMR (CDCl_3 , 400MHz) δ (ppm): 8.28 (m, 4H), 8.15 (m, 4H), 7.49 (t, 1H), 7.38 (m, 4H), 7.21 (t, 1H),

7.18 (dd, 2H), 6.97 (m, 4H), 5.81(m, 2H), 5.00 (m, 2H), 4.95 (m, 2H), 4.03 (t, 4H), 1.28-2.08 (m, 32H)

Characterization.

IR and NMR spectra were obtained by a Jasco 300E FT/IR and a Bruker DPX 200 MHz NMR spectrometers. The phase transition temperatures were determined by differential scanning calorimeter (NETZSCH DSC 200 F3). The DSC heating and cooling rates were of $10^\circ\text{C}/\text{min}$.

Optical textures were observed by a polarizing microscope(Zeiss, Jenapol) equipped with a camera and a thermo-control (Mettler FP82HT).

3. Results and discussion

Synthesis of banana-shaped monomer.

Banana-shaped monomer with ester linking group and the carbon number of terminal flexible group fixed to 11 was synthesized. The structures of compounds were characterized by ^1H NMR and FT-IR spectroscopy. The spectral dates were in accordance with the expected molecular formulas.

Thermal properties and optical textures.

The transition temperatures and enthalpy changes on 1st heating and cooling were summarized in Table 1, Figure 2 displayed the DSC curve of monomer(4a).

Melting temperature of monomer (4a) was 127°C with the enthalpy change of 25.29 J/g. The isotropic transition temperature of the monomer (4a) was 142°C with the enthalpy change of 0.964 J/g. Figure 3

shows the optical textures of the monomer taken at 125 °C and 110 °C on cooling.

4. Acknowledgements

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5. References

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Table 1. Transition temperature(°C) and enthalpy changes (J/g).

Monomer	Phase behavior
4a	Cr 53.7 (50.9)
	SmX ₁ 89.0 (7.53)
	SmX ₂ 129.0 (25.3)
	I 142.4 (0.96)

Cr = Crystalline phase, SmX = Smetic phase

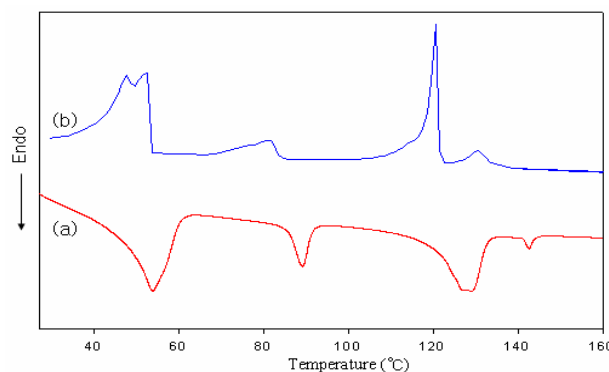
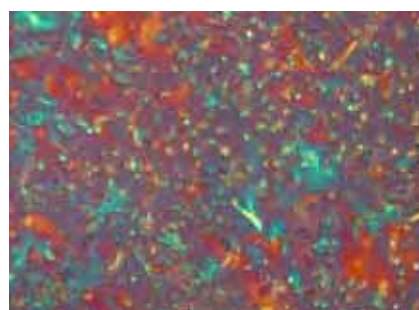
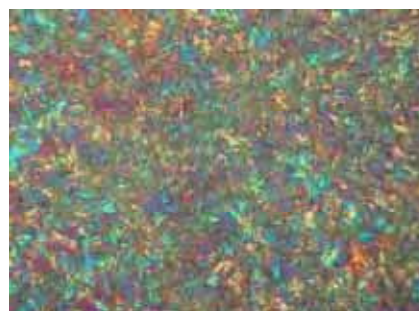


Figure 2. DSC thermograms for monomer (4a).
(a) heating ; (b) cooling.



(a)



(b)

Figure 3. Optical microscopic texture of monomer (4a) on cooling ; (a) at 125 °C ; (b) at 110