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Synthesis and Characterization of Three-Arm Star-Shaped Glassy Liquid Crystal Containing Biphenyl Esters

Salisu, A. A.
Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B. 3011, Kano, Nigeria
Email: aasalisu@yahoo.com

ABSTRACT

A new three arm liquid crystalline material containing **4**-Hydroxy-4`-[(p-alkoxybiphenyloxy) carbonyl] valeric acid and linked by flexible spacers tris[-4-(p-alkoxybiphenyloxy)carbonyl] valeric acid phloroglucinol ester has been synthesized and characterized by spectroscopic methods of analysis. The transition temperatures and phase behaviors were studied by Differential Scanning Calorimetry (DSC), Polarizing Optical Microscopy (POM) and X-Ray diffraction analyses. All the synthesized compounds exhibited enantiotropic nematic phase and the stability of the mesophase depends on the length of the terminal alkoxy group for the compounds studied.

Keywords: Glassy phase, Liquid crystal, Nematic phase, Star shaped, Vitrification

INTRODUCTION

Liquid crystals (LCs) are fascinating states of matter having certain properties characteristics of liquid with other typical of crystals. They are unique nanostructures with remarkable electronic and optoelectronic properties (Kumar 2005). LCs exhibit rheological behavior similar to those of liquids and anisotropic physical properties similar to those of crystalline solids in the same thermodynamically stable phase (KiliC and Cinar 2007). These materials are extremely diverse ranging from DNA to high strength synthetic polymers like Kevlar and from small organic molecules like alkylcyanobiphenyls used in displays to self-assembling amphiphilic soap molecules (Woltman *et al.* 2008).

Due to simultaneously possessing the optical anisotropy of the crystal and the fluidity of the liquid, LCs show many unique properties, including self-organizing nature, fluidity with long-range order, cooperative motion, anisotropy in physical properties (optical, electrical and magnetic), and alignment change by external fields at surfaces and interfaces (Bahadur 1992, Kumar 2005). These properties have enabled LCs to be widely used in liquid crystal display technologies and various photonic applications including optical data storage, optical switching, optical computers and integrated optical devices for communication (Yu and Ikeda 2004, Kumar 2005, Lutfor *et al.* 2005).

With the rapid development in liquid crystals science and technology, there is a growing interest in the synthesis and investigation of unconventional liquid crystals (Liu, *et al.* 2005). Star-shaped liquid crystal belongs to the class of unconventional liquid crystal having a small core and a few extended rigid mesogenic units, as liquid crystal arms. Looking at star-shaped molecular structure seems to be discotic however, due to the flexible spacers the compounds may exhibit nematic phases rather than columnar phase, with later preferred for the potential electro-optical application (Lee *et al.* 2002). Some of the star-shaped liquid crystals do not crystallize during cooling from the isotropic melt but vitrify to form glass-forming mesogens, which attracts much attention because glass-forming liquid crystal materials possess unique optical, mechanical and stable thermal properties (Bong *et al.* 2001).

Compared to polymers, low molecular weight star-shaped liquid crystals often possessed lower viscosity and this important property give good and fast orientation to the material, and allowed them to be readily processed into macroscopically ordered solid films (Liu *et al.* 2005). In addition to their application, unconventional star-shaped liquid crystals are especially, important for the theoretical understanding of the liquid-crystalline phenomenon (Lee and Yamamoto 2001). The transformation of a super cooled fluid state into a solid glassy material plays an important role in material science. Transport properties, thermodynamic and mechanical properties but also electric and optical properties are known to change significantly as the glass transition process takes place (Wandorff *et al.* 2003).

In the work described here we have successfully synthesized a new kind of star-shaped glass-forming liquid crystal materials, using 1,3,5-trihydroxybenzene as a core and [4-(P-alkoxybiphenyloxy)carbonyl]valeric acid as mesogenic units.

MATERIALS AND METHODS

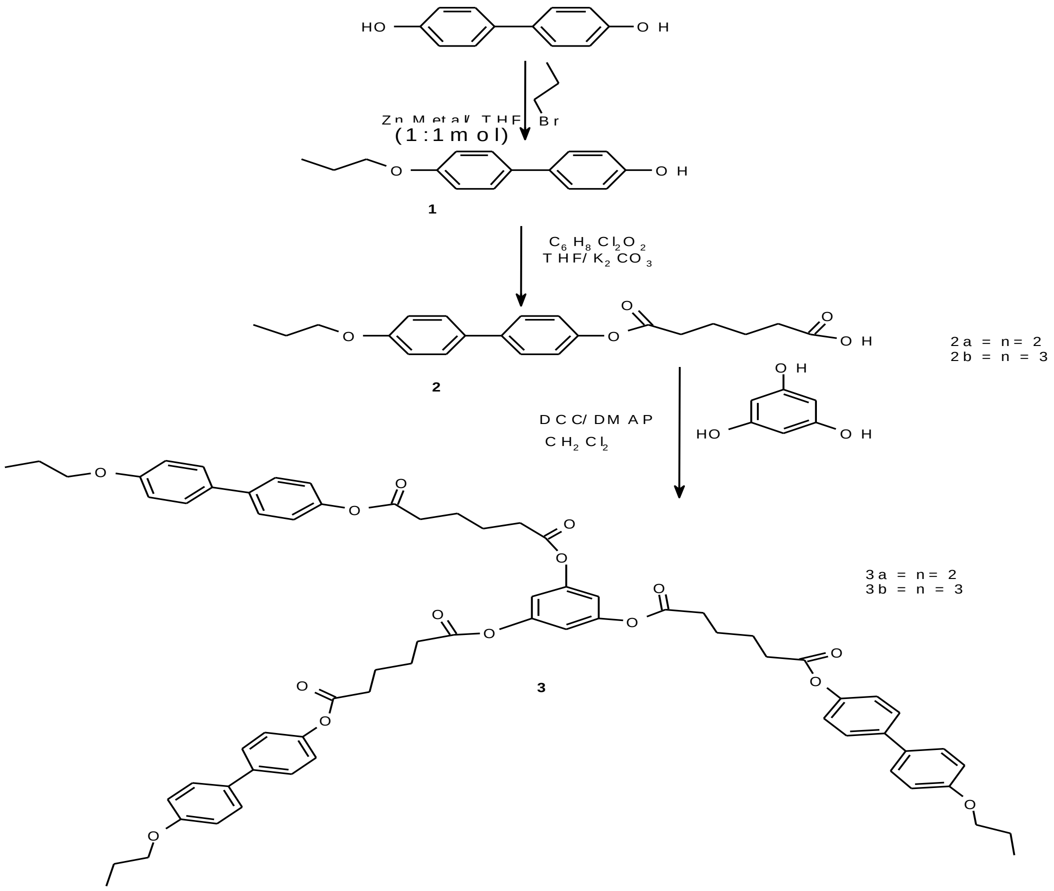
Materials

4,4`-Hydroxybiphenyl (Acros Organics), Methylbromide (BDH), Ethylbromide (BDH), Adipyolchloride (Fluka) 1,3,5-trihydroxybenzene (Fluka), Potassium carbonate (Marck) were used as purchased without any further purification. All other solvents and reagents were purified by standard methods. Silica gel 60 (230-460nm) was used for Column Chromatography; FT-IR spectra were measured on a BX spectrum II FT-IR spectrometer (Perking Elmer). ^{1}H NMR spectra (400 MHz) were recorded on a Jeol ECA 400 NMR spectrometer. Phase transition temperatures and thermodynamic parameters were determined using DSC 7 (Perkin Elmer) and DSC 8 (Diamond DSC, Perkin Elmer) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating and cooling rates were 10^0C min^{-1}. Phase transition temperatures were collected during the second heating and the second cooling scans. An Olympus (Leica, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe the phase transition temperatures and optical textures to analyze liquid crystal properties of the new material. The X-Ray measurement was performed using a nickel-filtered Cu-K$_{\alpha1}$ radiation with a Philips X-Ray diffractometer X`PERT PRO PW 3040 (PanAnalytical, Holland)

Methodology

Synthesis

The synthetic approach to the generation of the mesogenic units **2a** and **2b** and, star-shaped liquid crystals **3a** and **3b** are shown in Scheme 1. The corresponding yields and structural characterization data are summarized in Table 1. P-alkoxybiphenyl-4`-ol (**1a** and **1b**) and 4-Hydroxy-4`-[(p-alkoxybiphenyloxy) carbonyl] valeric acid (**2a** and **2b**) were synthesized according to a literature procedure [Meier *et al.* 2004], from excess adipoyl chloride with compound **1**.



Scheme 1: Synthetic route to the mesogenic units (2a and 2b) and the three arm star-shaped (3a and 3b) compounds

Typical procedure for compound **2b** in scheme **I** is as follows:

4-Hydroxy-4`-[(p-alkoxybiphenyloxy) carbonyl] valeric acid

P-alkoxybiphenyl-4`-ol (1.2g, 6.5mmol), dissolved in 20ml dry freshly distilled THF, was slowly added to a solution containing adipoyl chloride (1.81g, 100mmol) and 50 ml of THF. The reaction mixture was stirred and boiled for 8 h in a dry atmosphere. After cooling to room temperature, the mixture was poured into cold water and the resulting white precipitate was collected by filtration. This was crystallized from ethanol and dried at 60^0C in a vacuum oven to achieve a white solid of **2b** with a yield of 58%.

Bis[4-(p-alkoxybiphenyloxy)carbonyl] valeric acid phloroglucinol ester (3a** and **3b)

In a typical procedure, 4-Hydroxy-4`-[(p-alkoxybiphenyloxy) carbonyl] valeric acid (300mg, 8.82mmol**),** phlorglucinol (100mg, 2.94mmol), and DMAP (45.7mg, 0.82mmol) were added into a dried dichloromethane (100ml). After stirring the mixture for 30 min at room temperature, DCC (100mg, 8.82mmol) was added and the mixture was continuously stirred for 24 h. The reaction mixture was filtered off and the solvent was removed under reduced pressure. The product was dissolved in chloroform, extracted two-times with a solution of 5% acetic acid and water successively (Liu *et al.* 2005, and Zheng *et al.* 2007). The chloroform was removed under reduced pressure and the product was crystallized twice from methanol and three times with ethanol to result in compounds **3a** and **3b** with a yield of 25% and 38% respectively.

RESULTS AND DISCUSSION

Spectroscopic analysis

The spectroscopic analysis confirmed the predicted molecular structures of the mesogenic units **2a** and **2b** and three-armed star-shaped liquid crystals **3a** and **3b**.

Table 1: Yields and characterization of mesogenic units for the star-shaped liquid crystals

Compound	Yield (%)	IR (KBr)cm^{-1}	^{1}H NMR(CDCl$_3$,d/ppm)
2a	**55**	310–2560 (–OH in –COOH); 1763,1730,1715,(C=O 1604, 1509 (Ar)	1.88 (m, 4H); 2.65 (t, 4H); 3.97(s,3H);6.98–8.08 (m, 8H);10.80 (s, 1H);
2b	**52**	3250–2555 (–OH in –COOH); 1758, 1731, 1716, (-C=O); 1604, 1510 (Ar)	1.45 (t, 3H); 1.90 (m, 4H); 2.67 (t, 4H); 4.12 (q, 2H); 6.96–8.03m, 8H); 11.20 (s, 1H);
3a	**25**	2933, 2871 (CH$_3$,CH$_2$); 1759,1731(-C=O);1610, 1508 (Ar)	0.86 (m, 12H); 2.62 (t, 12H); 3.90(s,9H);7.01–8.10 (m, 27H);
3b	**38**	2953 2946, 2840 (CH$_3$,CH$_2$) 1756,1730,1606,1503(Ar)	0.48 (t, 9H); 1.87 (m, 12H); 2.63 (t,12H); 4.12 (q, 6H);

In the IR spectra of **2a** and **3a,** the absorption of –OH stretching vibration in carboxylic acid groups in the range of 3250–2555 cm^{-1} which was clearly identified in the spectrum of mesogenic unit **2b**, while the disappearance of the peaks of the –OH stretching vibration in the spectrum of three armed star-shaped liquid crystal **3b** was observed, indicating a successful esterification reaction.

In addition, compound **2b** was apparently different from **3b** in the sense that the former contained three -C=O stretching vibration absorption bands 1758, 1731, 1716 cm^{-1} representing Ar–O–CO–R, Ar–CO–O–R and –COOH, respectively. However, **2b** only had 1756, 1730 cm^{-1} two -C=O characteristic bands indicating a stretch vibration in different ester modes, Ar–O–CO–R and Ar–CO–O–R. The ^{1}H NMR Spectra of **2b** showed a peak of hydrogen on carboxylic acid group at 11.20 ppm. These results confirmed the existence of 1,3,5-trihydroxybenzene ester products, showing consistency with literature report (Liu *et al.* 2005).

Phase behavior of the Mesogenic Units

The liquid crystalline properties of the mesogenic units **2a** and **2b** were characterized using DSC and OPM. The DSC thermograms are presented in Table 2. In heating traces, both **2a** and **2b** exhibited two endothermic peaks. One peak occurred at higher temperature (138.9^{0}C) and it had large enthalpy change (69.5J/gK^{-1}) corresponding to the transition from solid crystal to the liquid crystalline phase (Table 2). The other peak occurred at lower temperature (Cr118.8^{0}C) and had small enthalpy change (48.4 J/gK^{-1}) corresponding to the transition from the liquid crystalline phase to isotropic liquid phase. In the cooling cycle, the thermograms also showed two sharp exothermic peaks: The first peak occurred due to transition from the isotropic state into liquid crystalline phase at higher temperature. The second peak occurred at transition from the liquid crystalline phase to crystalline phase at lower temperature. The mesogenic region was around 20 ^{0}C.

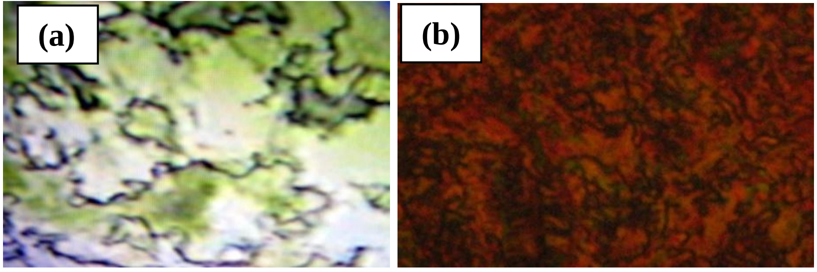
Table 2: Phase transition temperatures and enthalpies obtained from the DSC scans

Mesogenic Units	Transition temperature/^{0}C (corresponding enthalpy) changes/J gK^1), Heat/Cool
2a	Cr138.9(69.5)I/I129.6(8.2) N114.1(52.9)Cr 15.5
2b	Cr118.8(48.4)N123.9(5.5)/I120.8(13.8) N100.7(57.6)Cr20.1(5.1)
3a	Cr132.4(45.4)N141.2(3.9)I/I167.3(9.7) N112.7(54.7)Cr25.9 (10.2)
3b	Cr122.4(57.4)N131.2(2.7)I/I127.3(8.2) N106.4(64.7)Cr20.9 (8.8)

However, when **2a** was heated from room temperature, the DSC trace showed only one sharp endothermic peak at 138.9 ^{0}C indicating the melting temperature of the material. In cooling cycle from the isotropic liquid phase, the thermogram showed two exothermic peaks, at 129.6 ^{0}C and at 114.1 ^{0}C, with the region of liquid crystal phase at 15 ^{0}C. Furthermore, when the mesogenic units **2a** and **2b** were in the liquid crystal state, thread like texture, that is usually typical of the nematic phase, was observed using the crossed polarizer as shown in Figure 1. These data indicated that **2a** and **2b** were enantiotropic nematic liquid crystals, and **2a** was monotropic nematic liquid crystal with its mesogenic phase observed only on super cooling.

The thermal properties of three-armed star-shaped liquid crystals **3a** and **3b** evaluated by DSC were summarized in Table 2. The glass transition temperatures were in the region 13.2–21.9 ^{0}C. Both **3a** and **3b** had no specific melting point. It is a known fact that, liquid crystalline polymers, including side-chain liquid crystalline polymers, are atactic in their stereochemistry and their structural disorder in such systems often induces vitrification rather than crystallization during cooling (Grafe *et al.* 2005 and Liu *et al.* 2005). In contrast, low molecular mass compounds with high molecular order usually crystallize when the temperature is low enough.

In our studies, however, the DSC curves of these three-armed star-shaped liquid crystals **3a** and **3b** showed no crystallization, but vitrifying into a glass state, like most polymers, during cooling from the isotropic melt. Furthermore, the glass state was quite stable and no melting sharp peak was observed when the glass was reheated. This was probably due to steric hindrance which hindered the crystallization of these star-shaped molecules as reported for similar compounds (Liu *et al.* 2005).



(2a) (2b)

Figure 1: Optical Polarized Micrograph of 2b (200X). (a) Threadlike texture of 2b on heating to 120 ^{0}C. (b) Threadlike texture of 2b on cooling to 104 ^{0}C.

As presented in Table 2**, 3a** and **3b** were different from the mesogenic units **2a** and **2b.** The former two showed enantiotropic behaviour and a wide mesogenic region. On the heating traces, the mesogenic region of **3a** and **3b** was extended to 104.9 and 107.2 ^{0}C, respectively. Among them, **3a** exhibited the narrowest temperature range while, **3b** displayed the widest mesophase temperature range. The reason could be that the terminal polarity group played an important role during the liquid crystal phase formation and it maintained the molecular orientation through the acting forces of molecular induction and polarization. With the extension of terminal alkoxy chain (from n = 2 to 3), the molecular cooperative packing was enhanced and the structural anisotropy was increased. The phase transition temperatures displayed by these materials were reversible and did not change on repeated heating and cooling cycles similar to compounds reported by Liu *et al.* 2005. Texture analysis of the three-arm star-shaped liquid crystals **3a** and **3b** using OPM showed that **3a** and **3b** exhibited enantiotropic nematic phases on heating and cooling cycles respectively (Figure 2).

Considering **3b** for example, it was in liquid crystalline phase at room temperature due to its low glass transition, but with the increase in temperature, the sample flowed quickly, showing typical nematic thread like texture. However, the texture disappeared on heating the sample to 153 ^{0}C, where nematic droplets appeared followed by thread like texture when the isotropic state was cooled to 136 ^{0}C (Figure 2). The texture did not change until the cooling temperature reached 25^{0}C.

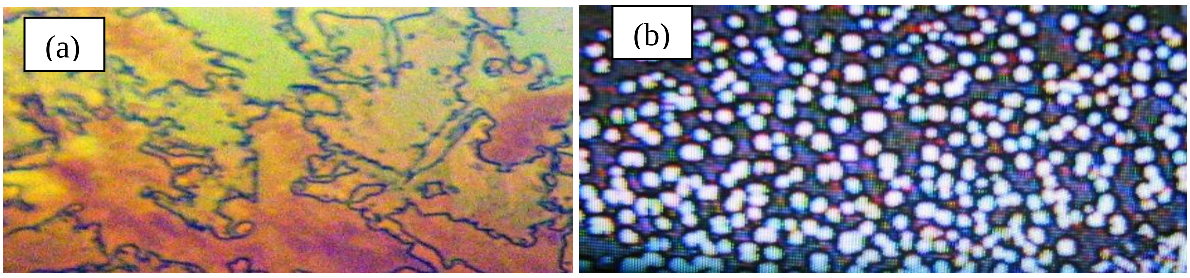


Figure 2: Polarized optical micrograph of 3b (200 X). (a) Threadlike texture of 3b at heating to 121^{0}C. (b) Droplets texture of 3b on cooling from isotropic liquid at 162^0 C.

In general, the nematic state is restricted to rod-like molecules which is a typical characteristics (for calamitic molecules) long axes roughly parallel or restricted to discotic molecules whose structures are similar to the calamitic nematic. The nematic phase was believed to be frozen due to high viscosity before crystallization (Cojocariu and Rochon, 2005).

CONCLUSION

A star-shaped liquid crystal containing biphenyl ester with phloroglucinol as the central core has been prepared and characterized by spectroscopic methods. The mesogenic unit **2a** exhibited enantiotrophic nematic liquid crystals characteristics where as the unit **2b** exhibited monotropic nematic liquid crystal characteristics on super cooling. The three-arm star-shaped **3a** and **3b** materials vitrified into glass during cooling and exhibited liquid crystal properties at room temperature in addition to exhibiting enantiotropic nematic thread like textures without undergoing crystallization at room temperature.

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