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Journal of Molecular Structure 741 (2005) 135-140



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Structure and properties of novel three-armed star-shaped liquid crystals

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Received 23 October 2004; revised 16 January 2005; accepted 18 January 2005 Available online 11 March 2005

Abstract

A series of novel three-armed star-shaped liquid crystals based on 1,3,5-trihydroxybenzene as a core and ω -[4-(*p*-alkoxybenzoloxy) phenoxycarbonyl]valeric acid as mesogenic arms were synthesized. Their chemical structures were confirmed by FTIR and ¹H NMR spectra, their mesomorphic properties and phase behavior were investigated using differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) measurements. The results show that the three-armed star-shaped liquid crystals exhibit a broad range of liquid crystalline phases at moderate temperature, no crystallization but vitrifying to form glass-forming mesogens during cooling from the isotropic melt. The formed crystals are glassy liquid crystals. The three-armed molecules are highly thermal stable and the mesomorphic ranges (ΔT) become wider as the terminal alkoxy chains become longer. Threadlike texture, a typical nematic phase, can be observed in the liquid crystalline state.

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Keywords: Liquid crystals; Three-armed star-shaped; Vitrify; Nematic phase

1. Introduction

Liquid crystals are fascinating materials with properties intermediate between those of solids and liquids. Conventional liquid crystals are composed of rod-like or discotic molecules. With the development of liquid crystals science and technology, there is a growing interest in the synthesis and investigation of unconventional liquid crystals [1-6]. Star-shaped liquid crystal is one kind of them, which usually has a small core and a few extended rigid mesogenic units as liquid crystal arms. At a glance, star-shaped molecular structure seems to be discotic, however, due to the flexible spacers the compound may exhibit nematic phases rather than columnar phase, which is preferred for the electrooptical application. 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 many special optical, mechanical and thermal stable properties [7–10]. Compared to polymers, low molecular weight star-shaped liquid crystals hold the lower viscosity and higher chemical purity and are readily processed into macroscopically ordered solid films [11]. In addition to their application, unconventional star-shaped liquid crystals are especially important for the theoretical understanding of the liquid-crystalline phenomenon.

In order to successfully synthesize a new kind of starshaped liquid crystal and meet the quality requirements for glass-forming liquid crystal materials, we use 1,3,5-trihydroxybenzene as a core and ω -[4-(*p*-alkoxybenzoloxy)phenoxycarbonyl]valeric acid as mesogenic units. Their chemical structures are confirmed by FTIR and ¹H NMR spectra. Their mesomorphic properties and phase behavior are investigated by using DSC, POM and X-ray diffraction measurements.

2. Experimental

2.1. Materials

p-Methyloxybenzoic acid, *p*-ethyloxybenzoic acid, *p*-propyloxybenzoic acid, *p*-benzenediol, 1,3,5-trihydroxybenzene, hexanedioic acid were obtained from Beijing

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^{0022-2860/\$ -} see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2005.01.057

Chemical Company (China) and used without any further purification. All other solvents and reagents were purified by standard methods.

2.2. Characterization

FTIR spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). ¹H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). Phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 (Netzsch, Germany) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating rates were 10 °C min⁻¹, and cooling rates were 10 °C min⁻¹. Phase transition temperatures were collected during the second heating and the first cooling scans. The thermal stability of the three-armed star-shaped liquid crystals under atmosphere was measured with a Netzsch TGA 209C thermograrimetric analyzer. A Leica DMRX (Leica, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe phase transition temperatures and optical textures to analyze liquid crystal properties of the mesogenic units and three-armed star-shaped liquid crystals. XRD measurements were performed using a nickel-filtered Cu K_{α} radiation with a DMAX-3A Rigaku (Rigaku, Japan) powder diffractometer.

2.3. Synthesis

The synthetic routes of the mesogenic units 2a-2c and star-shaped liquid crystals 3a-3c were shown in Scheme 1. Their yields and structural characterization were summarized in Table 1.

2.3.1. ω -[4-(p-alkoxybenzoloxy)phenoxy carbonyl]valeric acid (**2a**-**2c**)

4-Hydroxy-4'-[(*p*-alkoxy)benzoyloxy] phenyl (1) was synthesized according to a published procedure [12]. ω -[4-(*p*-Alkoxybenzoloxy)phenoxy carbonyl]valeric acid **2a–2c** was synthesized from excess adipyl chloride with compound 1. Typical procedure for compound **2b**: 4-hydroxy-4'-[(*p*-ethoxy)benzoyloxy] phenyl (5.16 g, 20 mmol), dissolved in 20 ml THF, was slowly added to a solution containing 18.3 g (100 mmol) of adipyl chloride, 5 ml of pyridine, 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 acidified with hydrochloric acid. The product was filtered and recrystallized from ethanol and dried in



(3a: n=1, 3b: n=2, 3c: n=3)

Scheme 1. The synthetic route of star-shaped liquid crystals.

 Table 1

 Yields and characterization of mesogenic units and star-shaped liquid crystals

Compound	n	Yield%	IR (KBr)/cm ⁻¹	¹ H NMR chemical shifts (CDCl3, <i>d</i> /ppm)
2a	1	55	3310–2560 (–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	2	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); 6.96–8.03 (m, 8H); 11.20 (s, 1H);
2c	3	44	3325–2550 (–OH in –COOH); 1755, 1728, 1714 (C=O); 1606, 1510 (Ar)	0.93 (t, 3H); 1.68 (m, 2H); 1.89 (m, 4H); 2.64 (t, 4H); 4. 05 (t, 2H); 6.99–8.08 (m, 8H); 10.70 (s, 1H);
3a	1	61	2933, 2871 (CH ₃ ,CH ₂); 1759, 1731 (C=O); 1610, 1508 (Ar)	1.86 (m, 12H); 2.62 (t, 12H); 3.90 (s, 9H); 7.01–8.10 (m, 27H);
3b	2	53	2946, 2840 (CH ₃ ,CH ₂); 1756, 1730, 1606, 1503 (Ar)	1.48 (t, 9H); 1.87 (m, 12H); 2.63 (t,12H); 4.12 (q, 6H); 6.98–8.06 (m, 27H);
3c	3	57	2939, 2851 (CH ₃ ,CH ₂); 1753, 1726 (C=O); 1605, 1501 (Ar)	0.93 (t, 9H); 1.67–1.83 (m, 18H); 2.65 (t, 12H); 4.10 (t, 6H); 6.98–8.06 (m, 27H);

a vacuum oven to achieve a white solid of **2b** with a yield of 52%.

2.3.2. $tri[\omega-4-(p-alkoxybenzoloxy)phenoxycarbonyl]$ valeric acid phloroglucinol ester (**3a–3c**)

In a general procedure, appropriate ω -[4-(*p*-alkoxybenzoloxy)phenoxy carbonyl]valeric acid 2a-2c (6.2 mmol, 3.1 equiv) was stirred in 25 ml of thionyl chloride and 0.5 ml of DMF was added as a catalyst. The solution was heated at reflux for 5 h whereby a clear solution was obtained. The excess of thionyl chloride was removed by vacuum and the acid chloride dried in vacuum for 1 h. Acid chloride was dissolved in 10 ml of dry THF, and 25 ml dry pyridine followed by adding 0.25 g (2 mmol, 1 equiv) of 1,3,5trihydroxy benzene to achieve esterification. The reaction mixture was stirred at 70 °C for 12 h in a dry atmosphere. After cooling to room temperature, the mixture was poured into 150 ml cold water and acidified with 6 N hydrochloric acid. The crude product obtained was collected by filtration and repeatedly washed with distilled water, followed by recrystallization from ethyl acetate/ethanol (1:1) to result in compounds **3a–3c** with a yield of 53–61%.

3. Results and discussion

3.1. Spectroscopic analysis

The spectroscopic analysis confirmed the predicted molecular structures of the mesogenic units 2a-2c and

Table	2				
Phase	transition	temperatures	of mesog	genic	units

three-armed star-shaped liquid crystals 3a-3c. Taking IR spectra of 2b and 3b as an example, the absorption of -OH stretching vibration in carboxylic acid groups in the range of $3250-2555 \text{ cm}^{-1}$ 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 threearmed star-shaped liquid crystal 3b was observed, indicating a successful esterifying reaction. In addition, 2b was apparently different from 3b that the former contained 1758, 1731, 1716 cm^{-1} three C=O stretching vibration absorption bands representing Ar-O-CO-R, Ar-CO-O-R and -COOH, respectively, but the latter 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. Analysed with ¹H NMR Spectra, **2b** but not **3b** showed a peak of hydrogen on carboxy group at 11.20 ppm. These results clearly indicated the existence of 1,3,5-trihydroxybenzene esters products.

3.2. Liquid crystalline behavior of mesogenic units

The liquid crystalline properties of the mesogenic units 2a-2c were characterized using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The results were shown in Table 2. Fig. 1 displayed the representative DSC thermograms. In heating trace, 2b and 2c both exhibited two endothermic peaks. One peak occurred at lower temperature (T_m) and it had large enthalpy change corresponding to the transition from crystal to the liquid crystalline phase. The other peak occurred at higher

Mesogenic units	n	Transition temperature/°C (corresponding enthalpy changes/ J g^{-1}), heating/cooling	ΔT_1^{a}	ΔT_2^{b}
2a	1	Cr138.9(69.5)I/I129.6(8.2)N114.1(52.9)Cr	-	15.5
2b	2	Cr118.8(48.4)N123.9(5.5)/I120.8(13.8)N100.7(57.6)Cr	5.1	20.1
2c	3	Cr122.4(57.4)N131.2(2.7)I/I127.3(8.2)N106.4(64.7)Cr	8.8	20.9

Cr, crystal; N, nematic; I, isotropic.

^a Mesophase temperature ranges on heating cycle.

^b Mesophase temperature ranges on cooling cycle.



Fig. 1. DSC thermograms of the mesogenic unit 2b.

temperature (T_i) and it had small enthalpy change corresponding to the transition from the liquid crystalline phase to isotropic liquid phase. The mesogenic region (ΔT) between $T_{\rm m}$ and $T_{\rm i}$ ($\Delta T = T_{\rm i} - T_{\rm m}$) of **2b** and **2c** was 5 and 9 °C, respectively. In cooling cycle from isotropic phase, the thermograms also showed two sharp exothermic peaks: one occurred at transition from isotropic to liquid crystalline phase at higher temperature (T_{ai}) and the other occurred at transition from liquid crystalline phase to crystal at lower temperature (T_c). The mesogenic region was around 20 °C. However, when 2a was heated from room temperature, the DSC trace showed only one sharp endothermic peak at 138.9 °C indicating the melting temperature($T_{\rm m}$). In cooling cycle from the isotropic liquid phase, the thermogram showed two exothermic peaks, T_{ai} at 129.6 °C and T_c at 114.1 °C, with the region of liquid crystal phase at 15 °C. In addition, when the mesogenic units 2a-2b were in the liquid crystal state, threadlike texture, the typical of nematic phase, was observed using the crossed polarizer as shown in Fig. 2. These data indicated that 2b and 2c were enantiotrpic nematic liquid crystals, and 2a was monotropic nematic liquid crystal with its mesogenic phase observed only on supercooling.

3.3. Thermal properties of three-armed star-shaped liquid crystals

The thermal properties of three-armed star-shaped liquid crystals 3a-3c evaluated by DSC were summarized in Table 3 and the representative DSC thermograms were shown in Fig. 3. The glass transition temperatures were at 13.2–21.9 °C and 3a-3c had no melting point. As we know, liquid crystalline polymers, such as side-chain liquid-crystalline polymers, are atactic and their systems disorder induces vitrification rather than crystallization during cooling. 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-3c 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.



Fig. 2. Polarized optical micrograph of **2b** $(200 \times)$. (a) Threadlike texture of **2b** at heating to 120 °C. (b) Threadlike texture of **2b** at cooling to 111 °C.

Thase transition competatores of star-shaped right crystars						
star-shaped liquid crystals	п	Transition temperature/°C (corresponding enthalpy changes/J g^{-1}), heating/cooling	ΔT_1^{a}	ΔT_2^{b}	$T_{\rm d}^{\rm c}$	
3a	1	g13.2 (0.2) ^d N86.3 (1.4)I/I84.1 (1.5)N7.7 (0.3) ^d g	73.1	76.4	353	
3b	2	g21.9 (0.3) ^d N126.8 (1.7)I/I125.6 (1.9)N17.1 (0.6) ^d g	104.9	108.5	349	
3c	3	g16.4 (0.6) ^d N123.6 (5.2)I/I121.9 (5.4)N11.3 (0.8) ^d g	107.2	110.6	357	

Table 3 Phase transition temperatures of star-shaped liquid crystals

g, glass state; N, nematic; I, isotropic.

^a Mesophase temperature ranges on heating cycle.

^b Mesophase temperature ranges on cooling cycle.

^c Temperature at which 5% weight loss occurred.

^d ΔC_p in J/(gk).

As summarized in Table 3, **3a–3c** were different from the mesogenic units **2a–2c** that they showed enantiotropic behaviour and a wide mesogenic region. On heating trace, the mesogenic region of **3a–3c** was extended to 73.1, 104.9 and 107.2 °C, respectively. Among them, **3a** exhibited the narrowest while **3c** 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=1 to 3), the molecular cooperative packing was enhanced and the structural anisotropy was increased.

The phase transition temperatures displayed in the Table 3 were reversible and did not change on repeated heating and cooling cycles. Meanwhile, TGA results showed that the temperatures were higher than 340 °C when 5% weight loss occurred (T_d), indicating a high thermal stability of synthesized star-shaped liquid crystals.

3.4. Texture analysis of three-armed star-shaped liquid crystals

Studies on the textures of three-armed star-shaped liquid crystals **3a-3c** using POM showed that **3a-3c**

exhibited enantiotropic nematic phases on heating and cooling cycles (Fig. 4). Taking star-shaped liquid crystal **3b** for example, it was in liquid crystalline phase at room temperature due to its low glass transition temperature, but with the increase of the temperature, the sample flowed quickly, showed typical nematic threadlike textures gradually. However, the texture disappeared at 127 °C, but nematic droplets appeard followed by threadlike texture when the isotropic state was cooled to 125 °C. The texture did not change until the temperature reached room temperature.

X-ray diffraction measurements can provide more detailed information on the liquid crystalline phase structures. The quenched samples of three-armed starshaped liquid crystals **3a–3c** were studied by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Data showed amorphous diffuse peaks at about 2θ of 20°, but no sharp peak in the lower Bragg angle region. This result suggested that **3a–3c** exhibited only nematic mesophases [13], which was consistent with their optical textures.

In general, the nematic state is restricted to rod-like molecules which spontaneously order with their (for calamitic molecules) long axes roughly parallel or restricted to discotic molecules whose structures are similar to the calamitic nematic, although in this case the short axes of



Fig. 3. DSC thermograms of the star-shaped liquid crystal 3b.



Fig. 4. Polarized optical micrograph of **3b** $(200 \times)$. (a) Threadlike texture of **3b** at heating to 98 °C. (b) Droplets texture of **3b** at cooling to 124 °C.



Fig. 5. Diagram of three-armed star-shaped molecules anisotropic structure in the nematic phase.

the molecules tend to lie parallel. The long rigid arms comparable to the calamitic mesogen in the symmetric star molecules, were found to be the driving force for the nematic phase in the three-armed star-shaped liquid crystals **3a–3c**. These linearly extended arms were attached to a small core with a longer flexible spacer derived from hexanedioic acid that the arm-to-arm interaction occured between and within molecules. As a result, the star-shaped molecules are capable of folding an anisotropic shape to give rise to the appearance of a nematic liquid crystalline order (Fig. 5).

4. Conclusion

In this work, a novel three-armed star-shaped liquid crystals 3a-3c has been synthesized. These molecules do not crystallize but vitrify to form stable supercooled mesophase when cooled so that they can be applied as glassy liquid crystals. The synthesized star-shaped liquid crystals 3a-3c show wide mesomorphic temperature ranges and high thermal stability. In addition, the mesomorphic temperature ranges increase as the terminal alkoxy chain extends and the liquid crystals exhibit threadlike optical texture, a typical nematic liquid crystal phase, in heating and cooling cycles.

Acknowledgements

The authors are grateful to National Natural Science Fundamental Committee of China and HI-Tech Research and development program (863) of China, National Basic Research Priorities Programme (973) of China, and Science and Technology Research Major Project of Ministry of Education of China for financial support of this work.

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