

# Synthesis and mesomorphism of novel star-shaped glassy liquid crystals containing pentaerythritol esters

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**Abstract**—A new class of star-shaped glassy nematic liquid crystals based on pentaerythritol as a flexible core and  $\omega$ -[4-(*p*-alkoxybenzoloxy)phenoxy]valeric acid as the side-chain mesogenic arms has been prepared. Their structures and mesomorphism have been investigated in detail.

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Glassy liquid crystals (GLCs), which do not crystallize upon cooling, but vitrify and form supercooled liquid crystalline phases are useful materials for fabrication of thermoelectrooptical storage displays and different optical components.<sup>1–3</sup> As a rule, GLCs can be divided into polymers<sup>4,5</sup> and low molecular mass compounds.<sup>6,7</sup> Compared with polymers, the main advantages of low molecular mass compounds are the lower viscosity and superior chemical purity, so low molecular mass GLCs hold a fast and good orientation, which can be readily processed into macroscopically ordered solid films.<sup>8</sup> As we know, the unconventional liquid crystals, with molecular structures deviating substantially from the simple rod-like shape, are many which can form GLCs such as branched compounds, derivatives of condensed aromatic rings like naphthalene, phenanthrene, *ortho*- or *meta*-substituted benzene derivatives. Among these low molecular mass GLCs, star-shaped glassy liquid crystals (SGLCs) are particularly attracted the attention, owing to their symmetrical molecular structures and interesting properties. The star-shaped structure usually has a small core and a few extended rigid mesogenic units as the side-chain liquid crystal arms, which is different from conventional rod-like or discotic molecules. But most star-shaped molecules having high molecular order usually crystallize, instead of vitrifying into a glassy state, during cooling from the isotropic melt.<sup>9,10</sup> Here we report the synthesis of a new class of

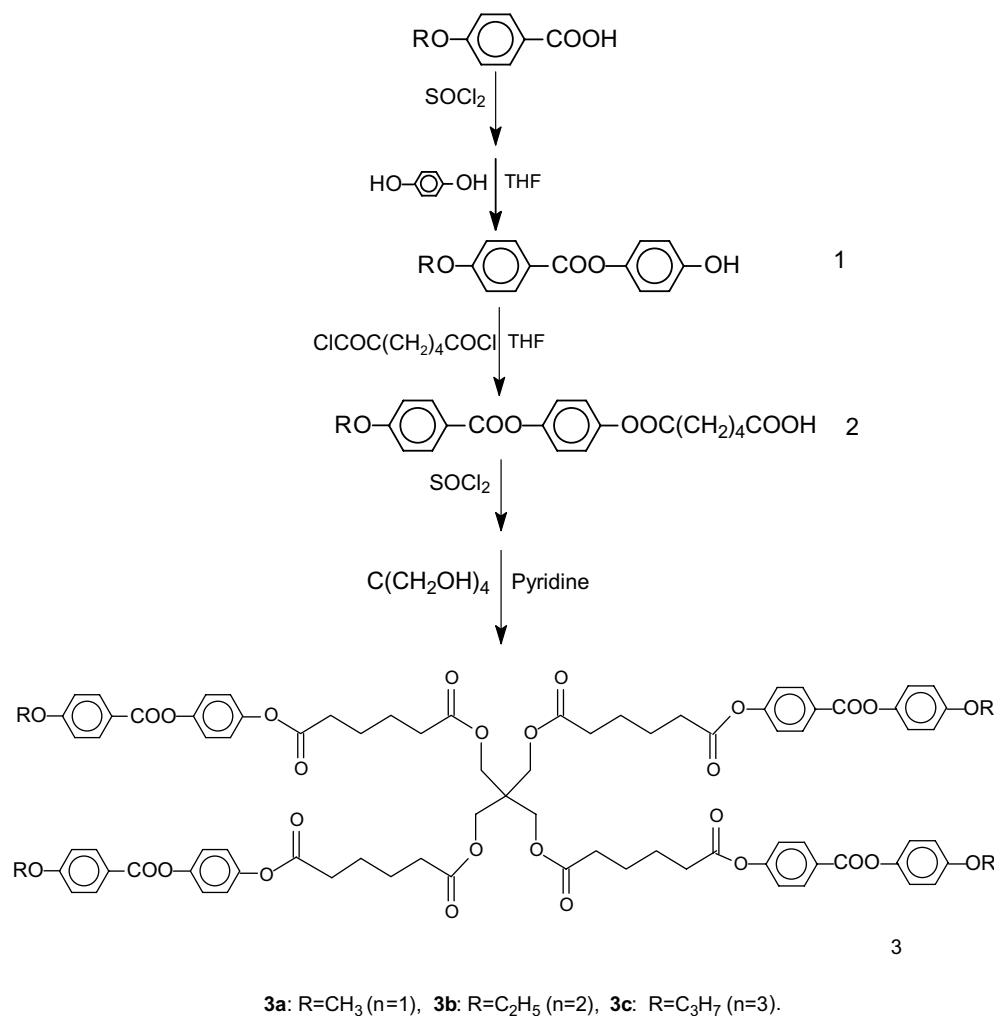
SGLCs, using pentaerythritol as a flexible core and  $\omega$ -[4-(*p*-alkoxybenzoloxy)phenoxy]valeric acid as the side-chain mesogenic arms, which do not crystallize upon cooling, but vitrify and form supercooled nematic phase.

The structure and synthetic route of SGLCs (**3**) were shown in **Scheme 1**. 4-Hydroxy-4'-[(*p*-alkoxy)benzoyloxy]phenyl (**1**) was synthesized according to a reported procedure,<sup>11</sup>  $\omega$ -[4-(*p*-alkoxybenzoloxy)phenoxy]valeric acid (**2**) was synthesized from excess adipyl chloride and compound **1**. Purified compound **2** was transformed into the corresponding acyl chloride and reacted with the appropriate pentaerythritol (molar ratio = 4.2:1) in pyridine for 16h stirring to give the desired compound **3** in reasonable yields (48–56%). Compound **3** showed good solubilities in common organic solvents and it was carefully identified by <sup>1</sup>H NMR, IR and elemental analyses.<sup>12</sup>

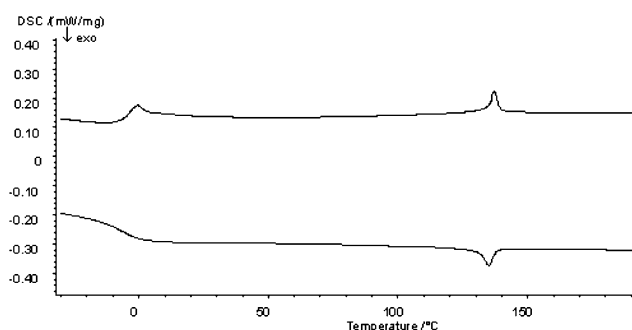
The thermal properties of **3** evaluated by DSC (differential scanning calorimetry) were summarized in **Table 1** and the representative DSC thermograms were shown in **Figure 1** (Netzsch DSC 204, equipped with a liquid nitrogen cooling system. Scan rate, 10 °C/min). As we know, polymers such as the side-chain liquid crystalline polymers are atactic,<sup>13</sup> their disordered systems induce vitrification rather than crystallization during cooling. But the DSC curves of these low molecular mass **3** showed that they did not crystallize during cooling from the isotropic melt, instead, vitrifying into a glassy state just like most polymers. Furthermore, the glassy state was quite stable, no sharp melting peak was observed

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



**Figure 1.** DSC thermograms of star-shaped glassy liquid crystal **3b**.

when we reheated the glass. This was due to the steric effect, the crystallization of these star-shaped molecules was hindered. As summarized in **Table 1**, with their high clearing points and low glass transition temperature, **3a–c** all showed the enantiotropic behaviour and a wide mesogenic region. On heating, the mesogenic region of **3a** was extended to 100.8°C compared with 136.4°C for **3b** and 141.2°C for **3c**. The reason was that the polarity of the terminal group played a quite important role during the liquid crystal phase formation. It made the

**Table 1.** Phase transition temperatures of star-shaped glassy liquid crystals

Star-shaped glassy liquid crystals	Transition temperature/°C (corresponding enthalpy changes/J g <sup>-1</sup> ) heating cooling	$\Delta T_1^a$	$\Delta T_2^b$	$T_d^c$
<b>3a</b>	$\frac{g - 2.0(0.3)^d N 98.8(2.1) I}{195.6(-2.2) N - 6.3(0.3)^d g}$	100.8	101.9	344
<b>3b</b>	$\frac{g 2.1(0.4)^d N 138.5(2.4) I}{1135.4(-2.5) N - 1.7(0.6)^d g}$	136.4	137.1	356
<b>3c</b>	$\frac{g - 5.5(0.3)^d N 135.7(1.8) I}{1133.2(-1.9) N - 8.6(0.8)^d g}$	141.2	141.8	350

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

<sup>a</sup> Mesophase temperature ranges on heating cycle.

<sup>b</sup> Mesophase temperature ranges on cooling cycle.

<sup>c</sup> Temperature at which 5% weight loss occurred.

<sup>d</sup>  $\Delta C_p$  in J/(gK).

molecular maintain orient order through the acting forces of molecular induction and polarization.<sup>14</sup> As the terminal alkoxy chain lengthened (from  $n = 1$  to 3), the molecular cooperative packing was enhanced and

the structural anisotropy increased. The phase transition temperatures displayed in Table 1 were reversible and did not change on repeated heating and cooling cycles. Meanwhile, TGA results showed that the temperatures when 5% weight loss occurred ( $T_d$ ) were higher than 340 °C, which revealed that the synthesized compound **3** had a high thermal stability.

The textures of **3** studied with POM (polarizing optical microscopy) were shown in Figure 2. The results showed that **3** exhibited typical nematic thread-like textures in their liquid crystal state.<sup>15</sup> The quenched samples of **3** were also studied by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). The amorphous diffuse peaks of  $2\theta$  was found at about 20°, and no sharp peak in the lower Bragg angle region was observed as shown in Figure 3. This result suggested that **3** exhibited only nematic mesophases, which was consistent with the optical textures. In general, the nematic state has been restricted just to the rod-like molecules, which spontaneously ordered with their long axes roughly parallel or to discotic molecules, which are similar in structure to the rod-like nematic, although in the later case the short axes of the molecules tend to lie parallel. The driving force for the nematic phase in this kind of SGLCs was found that, in the symmetric star-shaped molecules, the linearly extended arms were attached to a

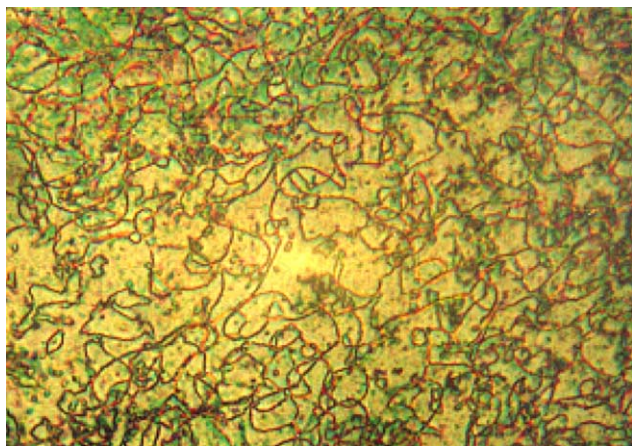


Figure 2. Polarized optical micrograph (200×) of **3b** at heating to 95 °C.

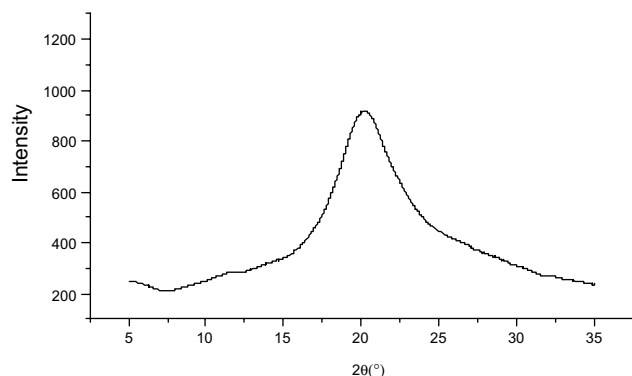


Figure 3. X-ray diffraction pattern of **3b**.

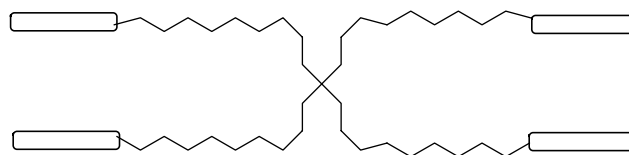


Figure 4. Diagram of star-shaped molecule anisotropic structure in the nematic phase.

small core with a longer flexible spacer derived from hexanedioic acid, the arm-to-arm interaction between neighbouring and within molecules existed. So the ability of such star-shaped molecules to fold into an anisotropic shape gave rise to the appearance of a nematic liquid crystalline order as shown in Figure 4.

In conclusion, we have synthesized a new kind of star-shaped glassy liquid crystals, which show a wide mesogenic region and high thermal stability. These compounds do not crystallize on cooling, but vitrify and form stable supercooled LC phase. Their optical texture is threadlike, typical of nematic LC phase.

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- All new compounds showed satisfactory spectroscopic data. Typical procedure for compound **3b**: 6.5 g (16.8 mmol) of compound **2b** were stirred in 25 mL of thionyl chloride and 0.5 mL of DMF as a catalyst was added. The solution was heated at reflux for 5 h whereby a clear solution was obtained. The excess of thionyl chloride were removed in vacuum and the acid chloride dried in vacuum for 1 h. For the esterification, the acid chloride was dissolved in 10 mL of dry THF and 25 mL dry pyridine and 0.54 g (4.0 mmol) of pentaerythriol were added. The reaction mixture was stirred at 70 °C for 16 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 precipitate was collected by filtration and washed with distilled water. The crude product was recrystallized from ethyl acetate/ethanol (1:1) to afford a white solid of compound **3b** in 52% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.48 (t, 12H, *J* = 6.3 Hz, CH<sub>3</sub>) 1.77–1.83 (m, 16H, CH<sub>2</sub>), 2.60 (t, 16H, *J* = 6.3 Hz, CH<sub>2</sub>COO), 4.02 (q, 8H, *J* = 6.3 Hz, CH<sub>2</sub>O), 4.17 (s, 8H, COOCH<sub>2</sub>), 6.90–7.20 (m, 24H, Harom), 8.12 (d, 8H,

*J* = 8.9 Hz, Harom); IR (KBr) 2923 (C–H); 1757, 1732, (C=O); 1605, 1510 (Ar); 1254, 1187 (C–O–C) cm<sup>-1</sup>. Anal. calcd for C<sub>89</sub>H<sub>92</sub>O<sub>28</sub>: C, 66.41; H, 5.76. Found: C, 66.28; H, 5.43.

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