Synthesis and Mesophase Behavior of Schiff Base Liquid Crystals with Long-chain Aliphatic-acid

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Abstract. Utilizing p-chloroaniline, p-hydroxybenzaldehyde and aliphatic diacids with different chain length as raw materials, the Schiff base liquid crystals Cl-SBPA4, Cl-SBPA6, Cl-SBPA8 and Cl-SBPA10 were synthesized by condensation and esterification. Their chemical structures were confirmed by FTIR and 1H NMR spectra. The mesophase behaviors were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The influence of molecular structure on mesophase behavior and optical property were discussed. The results demonstrated that Cl-SBPA4 exhibited smectic mosaic texture, Cl-SBPA6 and Cl-SBPA8 showed nematic droplet and schlieren texture, while Cl-SBPA10 had no mesomorphic phases. With the increase of the length of flexible chain, their melting transition (T_m) and crystallization temperature (T_c) exhibited a trend of decreasing first and then going up.

1. Introduction
Liquid crystal materials have attracted much attention due to their unique optical and electrical properties in recent years [1-3]. They are widely used in many types of applications in our daily life, such as liquid crystal displays, smart phones and other electronic devices [4-6]. Among them, Schiff base liquid crystals are very popular. Schiff base mainly refers to a class of organic compounds containing imide characteristic group (CH=N). Though the Schiff base group provides a stepped core structure, it retains molecular linearity, while the strong polarity and rigidity of imine bond lead to its stronger intermolecular interaction, the Schiff base compounds are prone to exhibiting the liquid crystal phase [7, 8]. The results show that Schiff base liquid crystals show good performance in liquid crystal display field [9, 10].

2. Experimental
2.1. Materials
p-chloroaniline, phenol, hexanedioic acid, octandioic acid, sebacic acid, dodecanedioic acid, N,N’-dicyclohexylcarbodiimide (DCC) and 4-dimethylamino-pyridine (DMAP) were bought from Shanghai Chemical Industry Company (China). All other solvents and reagents were purified by standard methods.

2.2. Characterization
FTIR spectra were measured on a Nicolet 510 FTIR spectrometer. 1H NMR spectra (300MHz) were recorded on a Varian WH-90PFT spectrometer. Phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 equipped with a liquid nitrogen cooling system under nitrogen atmosphere at a heating and cooling rate of 10 °C/min. A Leica DMRX polarizing optical microscope equipped with a Linkam THMSE-600 hot stage was used to observe
phase transition temperatures and optical textures.

2.3. Synthesis

The synthetic routes of the intermediate and the Schiff base liquid crystals were shown in Scheme 1.

A ethanol solution of p-chloroaniline (10.0 mmol) was added dropwise to a solution of p-hydroxybenzaldehyde (10.0 mmol) in ethanol. The mixture was stirred at 80°C temperature for 3 h. The yellow precipitate was collected by filtration and washed with ethanol to yield the intermediate Cl-SBP. The subsequent esterification of Cl-SBP (20.0 mmol) with excess aliphatic diacids (50.0 mmol) THF with DCC (25.0 mmol) and DMAP (2.0 mmol), stirred at room temperature for 20 h. The precipitated N, N-dicyclohexylurea (DCU) was removed by filtration and the solvent was evaporated. The solid residue was purified by recrystallisation from ethanol to afford the desired products Cl-SBPA4, Cl-SBPA6, Cl-SBPA8 and Cl-SBPA10.

3. Results and Discussion

3.1. Structural Characterization

The structure of the predicted molecular structures of the Schiff base liquid crystals were characterized by FT-IR, 1H NMR and elementary analysis. The absorption peaks of N-H stretching vibration in p-chloroaniline at 3235, 3215 cm⁻¹ disappeared, while the absorption of -OH and -CH=N- stretching vibration of Cl-SBP at 3300 cm⁻¹ and 1624 cm⁻¹ appeared respectively, indicated condensation reaction completely. Taking IR spectra of Cl-SBPA4 as an example, it showed characteristic stretching bands at about 3180-2560 cm⁻¹ attributed to -OH in carboxylic acid, strong peaks at 1735 cm⁻¹ and 1702 cm⁻¹ attributed to ester C=O and carboxylic acid C=O, weak peak at 1623 cm⁻¹ associated to -CH=N-. These indicated that the esterification achieved. The specific data were as follows: IR (KBr, cm⁻¹): 3180-2560 (O-H); 2947, 2842 (C-H); 1735, 1702 (C=O); 1623 (CH=N); 1580, 1510, 1450 (Ar-). 1H-NMR (CDCl₃, TMS, δ, ppm): 1.53~1.93 (m, 4H, –CH₂CH₂-), 2.17~2.32 (t, 2H, -CH₂-), 2.45~2.60 (t, 2H, -CH₂-), 6.96~7.22 (m, 6H, Ar-H), 7.36~7.78 (m, 2H, Ar-H), 8.47 (s, 1H, -CH=N), 10.21 (s, 1H, -COOH). In addition, with the increase of carbon chain, the intensity of C-H absorption peak at 2950, 2850 cm⁻¹ in the product increased. IR of the desired Schiff base liquid crystals were displayed in Figure 1.
3.2. Thermal Properties

The thermal properties of the Schiff base liquid crystals, obtained with DSC, were summarized in Table 1. The thermograms were presented in Figure 2. All phase transitions were reversible and did not change on repeated heating and cooling cycles.

Table 1. Transition temperature (°C) and mesogenic range for the Schiff base liquid crystals

| Sample    | Phase transitions(°C) | Heating/cooling |
|-----------|------------------------|-----------------|
| Cl-SBPA4  | Cr 151.3 S 161.5 I / I 101.1 S 94.3 Cr | 8.2/6.8         |
| Cl-SBPA6  | Cr 129.4 N 160.2 I / I 95.2 N 82.1 Cr | 30.8/13.1       |
| Cl-SBPA8  | Cr 121.9 N 131.7 I / I 105.4 N 73.8 Cr | 9.8/31.6        |
| Cl-SBPA10 | Cr 125.2 I / I 88.5 Cr |                 |

The figures marked that Cl-SBPA4, Cl-SBPA6 and Cl-SBPA8 showed the enantiotropic behavior, while Cl-SBPA10 had no mesomorphic phases. $T_m$ of them decreased first, from 151.3°C to 129.4°C to 121.9°C, and then increased to 125.2°C, with the length of alkyl chains growing. The temperatures of crystalline transition ($T_c$) displayed the similar trend. It is generally known that the rigidity and polarity of molecules decrease with the increase of carbon chain, while the molecular weight increases. As a result, $T_m$ and $T_c$ of the Schiff base liquid crystals showed the above trend of change. The
temperatures from liquid crystal to isotropic liquid phase transition \( (T_i) \) for Cl-SBPA4 and Cl-SBPA8 were obtained from POM. The endothermic peaks corresponding to \( T_i \) were not observed in the DSC curves may be due to the fact that the enthalpy change of them were too small to be detected.

3.3. Optical Properties
The optical textures of the Schiff base liquid crystals were investigated by polarizing optical microscope (POM) with hot stage, which was used to observe the characteristic textures for identification of phases. Their representative textures are shown in Figure 3. When Cl-SBPA4 was heated to \( T_m \), the mosaic texture appeared. The texture didn’t disappear until the sample changed into isotropy at 162.0°C. On cooling, the mosaic texture appeared again at 101.5°C. Mosaic texture is the typical texture of smectic phase. The XRD pattern of Cl-SBPA4 showed a sharp and a diffuse Bragg reflection in the low-angle region and the broad-angle region, respectively, which suggested the smectic phase arrangement. When Cl-SBPA6 and Cl-SBPA8 were heated to their \( T_m \), the schlieren defect with fourfold brushes presented, which were the typical textures of nematic phase, when they were cooled from isotropic, the nematic droplet texture displayed and gradually coalesced and showed nematic schlieren texture. The texture did not disappear until they crystallized. When Cl-SBPA10 was heated to \( T_m \), no liquid crystal texture appeared, it went directly into isotropic liquid phase. On cooling, it was crystallized directly from the liquid state.

![Figure 3](image)

**Figure 3.** Polarized optical micrographs (200×) of Cl-SBPA4, Cl-SBPA6 and Cl-SBPA8 (a) Cl-SBPA4, heating to 155.6 (b) Cl-SBPA6, heating to 142.4 (c) Cl-SBPA8, cooling to 102.5 (d) Cl-SBPA8, cooling to 92.8

4. Conclusions
A Class of Schiff Base Liquid Crystals with p-chlorine as terminal group and different long-chain aliphatic acid on the other side of the imine bond were synthesized and characterized. \( T_m \) or \( T_c \) of them decreased first and then increased with the length of alkyl chains growing. They were enantiotropic thermotropic liquid crystals, except Cl-SBPA10. Among them, Cl-SBPA4 appeared mosaic texture which was the typical texture of smectic phase, Cl-SBPA6 and Cl-SBPA8 displayed droplet and schlieren textures which were the typical textures of nematic phase.
5. Acknowledgements
This work was financially supported by the Fundamental Research Funds for the Central Universities (N110705001) and National Training Program of Innovation and Entrepreneurship for Undergraduates (181036).

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