Preparation and Study of Multi-Arm Azo Chiral Liquid Crystal Macromolecules

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Abstract. Utilizing 4-methoxyaniline, aliphatic diacid with different chain length, 4-hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid and cholesterol as raw materials, nine novel liquid crystal macromolecule were synthesized by diazotization and condensation reaction. We confirmed their molecular structure by IR spectra and observed their mesophase behaviors through differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). We found that all liquid crystal macromolecule had unique texture of cholesteric phase and summarized the conclusions of which liquid crystal properties were influenced by number of liquid crystal arms and strength of flexible chain length.

1. Introduction
Cholesteric liquid crystals which have chiral structure, own some unique properties of periodic arrangement and helical structure[1]. Due to the unique characteristics of reverse trans-cis-isomerization under light irradiation, azo liquid crystals have drew much attention[2-4]. Cholesteric liquid crystals and azo liquid crystals are two kinds of liquid crystals with excellent properties and have high application value as important soft materials[5]. They are widely used in optical storage, optical sensors, optical switches, photoelectric devices and other fields[6-11]. As it was reported, there are few studies on azo chiral liquid crystal macromolecule at home and abroad[12]. What we did is to synthesize nine novel azo chiral liquid crystal macromolecule and provide scientific data for study.

2. Experimental
2.1.Materials
4-methoxyaniline, phenol, hexanedioic acid, octandioic acid, sebacic acid, 4-hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic 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. 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 mesogenic unit B, the intermediate C_{11}-C_{33} and the azo liquid crystal macromolecules D_{11}-D_{33} were shown in Scheme 1.

The multi-arm azo chiral liquid crystals were prepared by the same synthetic method, so the synthesis of D_{33} was given as an example. Under ice-water bath, 4-substituted aniline and HNO_{2} (NaNO_{2}+HCl) diazotization, then coupled with phenol under alkaline conditions, got the orange powder A. Dissolved sebacic acid, DCC and DMAP with THF and poured into a round bottom flask.
for reaction for half an hour, then added A, stirred for 36 h at room temperature in a dry atmosphere, 2 mL of H₂O was added to stop the reaction. After filtration and recrystallization, the mesogenic unit B₃ was obtained. C₃₃ was synthesize by the interaction of B₃ with 3,4,5-dihydroxybenzoic acid, and the target product D₃₃ was obtained by the reaction of C₃₃ with cholesterol.

3. Results and Discussion

3.1. Structural Characterization

![Figure 1. FT-IR spectrum of D₃₃.](image)

The spectroscopic analysis confirmed the predicted molecular structures of the azo liquid crystal compound D. Taking IR spectra of D₃₃ as an example, the absorption peaks of -OH stretching vibration in carboxylic acid at 3230-2500 cm⁻¹ and the absorption peak of C=O stretching vibration in carboxylic acid at 1705 cm⁻¹ disappeared, The results showed that the multibrachial azo intermediate was completely reacted with cholesterol. IR of D₃₃ was displayed in figure 1. The position of the infrared absorption peak of D₃₃ was shown in the Table 1.

| Wavenumbers (cm⁻¹) | Absorption strength | Attribution of peaks       |
|-------------------|--------------------|---------------------------|
| 2928/2849         | ms                 | -C-H-                     |
| 1761              | s                  | C=O                       |
| 1601-1494         | s                  | -C=C- (benzene ring)      |
| 1410              | w                  | -N=N-                     |

*s: Strong absorption; ms: Medium absorption; w: Weak absorption.

3.2. Thermal Properties

The thermal properties of multi-arm azo chiral liquid crystal macromolecules, obtained by DSC, were listed in Table 2. All phase transitions were reversible and did not change on repeated heating and cooling cycles.
Table 2. Phase transition temperature of multi-arm azo chiral liquid crystal macromolecules.

| Sample  | Phase transitions(°C) Heating/cooling | ΔT Heating/cooling ΔT₁/ΔT₂(°C) |
|---------|---------------------------------------|---------------------------------|
| D₁₁     | Cr 188.2 Ch 243.5 I / I 1235.9 Ch 137.5 Cr | 55.3/98.4                      |
| D₁₂     | Cr 169.5 Ch 215.7 I / I 1210.2 Ch 129.3 Cr | 46.2/80.9                      |
| D₁₃     | Cr 142.0 Ch 181.3 I / I 1173.5 Ch 115.6 Cr | 39.3/57.9                      |
| D₂₁     | Cr 145.9 Ch 168.5 I / I 1159.5 Ch 122.6 Cr | 22.6/36.9                      |
| D₂₂     | Cr 131.9 Ch 149.4 I / I 1133.8 Ch 98.5 Cr | 17.5/35.3                      |
| D₂₃     | Cr 138.6 Ch 150.3 I / I 144.7 Ch 110.0 Cr | 11.7/34.7                      |
| D₃₁     | Cr 159.0 Ch 193.5 I / I 186.3 Ch 127.3 Cr | 34.5/59.0                      |
| D₃₂     | Cr 145.2 Ch 169.8 I / I 158.7 Ch 113.5 Cr | 24.6/45.2                      |
| D₃₃     | Cr 141.5 Ch 159.6 I / I 152.8 Ch 112.2 Cr | 18.1/40.6                      |

Cr: crystal; Ch: cholesteric; I: isotropic.
ΔT₁: mesogenic range in heating; ΔT₂: mesogenic range in cooling.

These results indicated that the number and rigidity of the mesogenic arms had significant impact on mesomorphic behavior. With the length of alkyl chains growing, Tₘ, Tᵢ, Tᵢₐ, and Tᵢₖ of D₁₁-D₁₃ (D₁ series) decreased. (Tₘ: melting point; Tᵢ: the temperatures from liquid crystal to isotropic liquid phase transition; Tᵢₐ: the temperatures from isotropic liquid phase to liquid crystal transition; Tᵢₖ: the temperatures of crystalline transition) The reason was that the longer the flexible spacer, the lower the molecular rigidity, which is not conducive to the stable existence of liquid crystal state. D₃₁-D₃₃ (D₃ series) displayed the similar trend. The mesogenic range (ΔT) both in heating and cooling decreased as the length of alkyl chains growing, while ΔT₂ was bigger than ΔT₁, which rule applies to all series. The result shows that the mesogenic range of D₁ series is the widest and the mesogenic range of D₂ series is the narrowest. This result is influenced by many factors such as molecular weight, molecular arrangement regularity, rigidity and the length to diameter ratio of molecules.

3.3. Optical Properties

The optical textures of D₁₁–D₃₃ 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 2. When heated sample D₁₁ to 188.2°C until it melted, the textures of focal cone texture, which are the typical textures of cholesteric phase, were observed in the mesogenic region. The textures did not disappear until the temperature reached 243.5°C, and the sample became isotropic completely. For D₁₂, D₂₁, they showed the typical focal cone texture like D₁₁ during heating process as shown in figure 2. (a), (b), while D₃₂ showed cholesteric oil streaks texture as shown in figure 2. (c). When cooled D₁₁ from isotropic to liquid crystal state, it exhibited droplet texture at 241.2°C which were shown in figure 2. (d) and then gradually turned into focal cone texture. When cooled D₂₂ and D₃₃ separately to 117.6°C and 138.5°C, D₂₂ exhibited broken focal cone texture while D₃₃ showed cholesteric fingerprint texture as shown in figure 2. (e) and (f). The texture did not disappear until the temperature dropped to the crystallization temperature. The POM results indicated that D₁₁-D₃₃ were cholesteric thermotropic enantiotropic liquid crystal macromolecules.
4. Conclusions
Nine multi-arm azo chiral liquid crystal macromolecules (D11-D33) with different length and number of mesogenic unit were synthesized and characterized. They were enantiotropic thermotropic liquid crystals and displayed focal conic, oil streaks, fingerprint texture of cholesteric phase. Compared with the mesogenic unit, the mesogenic range of the target product was widen, which both in heating and cooling decreased as the length of alkyl chains growing, while $\Delta T_2$ was bigger than $\Delta T_1$. Length to diameter ratio of molecules, number and rigidity of liquid crystal units had obvious influence on the liquid crystal properties of azo liquid crystal macromolecules.

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6. References
[1] Yang X F, Han J L, Wang Y F and Duan P F 2019 J. Chem. Sci. 10(1) 172-178
[2] Li Y, Liu Y J and Luo D 2019 J. Mater Chem. C 7 15166-15170
[3] Pedersen T G and Johansen P M 1997 J. Phys. Rev. Lett 79(13) 2470-2473
[4] Seki T, Yokoi M, Fukuda R I, Hirai H and Yamaji T 1995 J. Mol. Cryst. Liq. Cryst. 267(1) 429-434
[5] Kim Y and Tamaoki N 2016 J. ACS Appl. Mater. Interfaces 8(7) 4918-26
[6] He W L, Li M, Liu S Q, Wei M G, Liu C, Li L L, Yang Z, Wang D and Cao H 2017 J. Liq. Cryst 45(3) 370-380
[7] Pang X L, Lv J A, Zhu C Y, Qin L and Yu Y L 2019 J. Adv. Mater. 31(52) e1904224
[8] Li M H, Auroy P and Keller P 2000 J. Liq. Cryst 27(11) 1497-1502
[9] Holme N C R, Ramanujam P S and Hvilstede S 1996 J. Opt. Lett. 21(12) 902-4
[10] Toshchevikov V, Saphiannikova M and Heinrich G 2009 J. Phys. Chem. B 113(15) 5032-5045
[11] Serak S V, Tabiryan N V and Assanto G 2012 J. Mol. Cryst. Liq. Cryst. 559(1) 202-213
[12] Téllez M D G, Navarro-Rodriguez D and Larios-Lopez L 2017 J. Mol. Cryst. Liq. Cryst. 647(1) 269-278