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Syntheses and room mesomorphic properties of novel gallic trimer and tetramer based on acylhydrazone structures

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ABSTRACT

Two novel gallic trimer **7** and tetramer **8** based on acylhydrazone structures were designed and synthesized in yields 76% and 81%, respectively. Their structures were confirmed by ^{1}H NMR, ESI-MS, and elemental analysis. Their mesomorphic properties were investigated by DSC, POM, and XRD analyses. The mesomorphic results suggested that they possessed good room-temperature columnar liquid crystalline property with wide range of mesomorphic temperature. The ranges of mesomorphic temperatures for compounds **7** and **8** were as wide as 115°C and 124°C, respectively.

KEYWORDS

Acylhydrazone; gallic; mesophase; synthesis

Introduction

In recent years, columnar liquid crystals have received considerable attention for various potential applications such as organic light-emitting diodes, organic photovoltaic cells, organic field-effect transistors, gas sensors, and photocopying machines [1–4]. Among various columnar liquid crystals, liquid crystal oligomers were paid much attention due to the physical properties of liquid crystalline oligomers, which were significantly different from those of conventional low molar mass liquid crystals. The liquid crystalline oligomers were ideal model compounds for polymers or networks due to the striking similarities in their transitional behaviors as well as their ease of purification and characterization, and some of them provided and stabilized a variety of fluid phases with fascinating functions. Further, an oligomeric approach provided a wide flexibility in molecular design towards multifunctional liquid crystals. For example, series of liquid crystal oligomers based on triphenylene dimers, trimers, and tetramers were investigated by Kumar, Imrie, Prasad, etc. [5–13]. Lately, gallic ethers or their analogues with three long aliphatic chains on its phenolic groups were seen as good structural units to construct novel columnar LCs by connecting with large conjugated aromatic core. For instance, the saddle-shaped tetraphenylenes with peripheral gallic esters displaying columnar mesophases were described by Laschat's group [14]. Detert reported the syntheses and mesomorphic properties of some tristriazolotriazines derivatives with 1,2-bis-substituted or 1,2,3-tri-substituted alkoxy side chains on phenyl groups [15, 16]. Our groups also presented two gallic-perylene-gallic trimers with interesting mesomorphic properties

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[17]. Nevertheless, comparing with the extensive studies on triphenylene oligomers, the varieties and amounts of columnar liquid crystals based on gallic oligomers were less so far. In this paper, we designed and synthesized novel gallic trimer and tetramer based on acylhydrazone structures, and investigated their mesomorphic properties. The results suggested that these gallic oligomers exhibited good room-temperature columnar liquid crystalline property with wide ranges of mesomorphic temperatures, which was seldom observed for gallic liquid crystals.

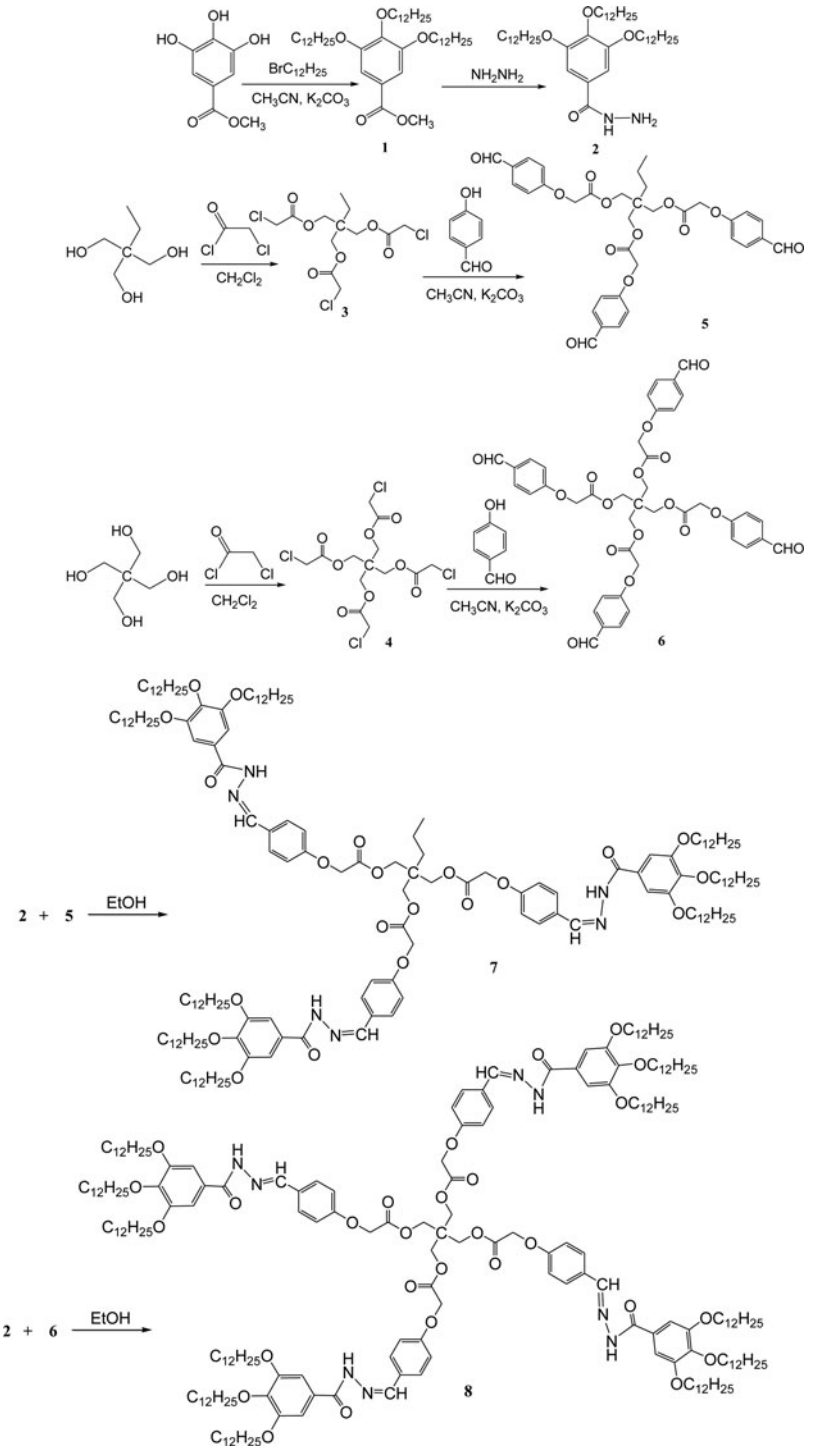
Results and discussion

Synthesis and characterization

The synthetic routes of gallic trimer and tetramer **7** and **8** were shown in Scheme 1. The gallic hydrazide derivative **2** was prepared by reacting methyl gallate with bromodecane and then hydrazinolysis with hydrazine hydrate in yield of 82% [18]. Also, by treating trimethylolpropane or pentaerythrotol with chloroacetyl chloride and subsequently reacting with *p*-hydroxybenzaldehyde, the derivatives with aldehyde groups **5** and **6** were prepared in yields of 80% and 85%, respectively. Further, by refluxing compound **2** with compound **5** or **6** in EtOH, the target gallic trimer **7** and tetramer **8** were obtained conveniently in the Schiff-base condensation in yields of 76% and 81%, respectively. The structures of all new compounds were well confirmed by elemental analysis, ESI-MS, and ^{1}H NMR spectra. One can see that, although gallic trimer and tetramer **7** and **8** possess no large rigid aromatic structures as cores, they have multiple rigid aromatic Schiff-base structures, which are similar to large rigid aromatic core and also favorable for the mesomorphic properties.

Mesomorphic studies

The mesomorphic behaviors of compounds **7** and **8** were preliminarily investigated by DSC. The results were shown in Fig. 1 and Table 1. It could be seen that both compounds **7** and **8** exhibited two endothermic peaks at 0.4°C (or –23.3°C) and 115.7°C (or 101.3°C), respectively, on second heating. On cooling, two exothermic peaks were observed at 94.5°C and –5.1°C for compound **7**, and at 93.1°C and –26.3°C for compound **8**, respectively. Also, the observation under POM suggested that two phase transitions of solid state-mesophase and mesophase-isotropic phase were observed for compounds **7** and **8** on heating and cooling. The phase transfer temperatures were in agreement with the endothermic peaks and exothermic peaks of DSC approximately, respectively. Especially, compounds **7** and **8** exhibited focal-conic fan textures on cooling as shown in Fig. 2, indicating that they were the columnar liquid crystals. These stable mesomorphic textures of compounds **7** and **8** existed at room temperature for several days. Moreover, it could be seen that the mesophase temperatures were 0.4∼115.7°C for compound **7** and –23.3∼101.3°C for compound **8**, indicating that they are excellent room-temperature columnar liquid crystals. The ranges of mesomorphic temperatures for compounds **7** and **8** were as wide as 115°C and 124°C, respectively. The tetramer **8** exhibited wider range of mesomorphic temperature and lower temperature of mesophase than that of trimer **7**, which could be attributed to the more gallic units favoring for the mesomorphic properties. These columnar liquid crystals were further confirmed by XRD analysis.



Scheme 1. Synthetic routes of gallic trimer and tetramer **7** and **8**.

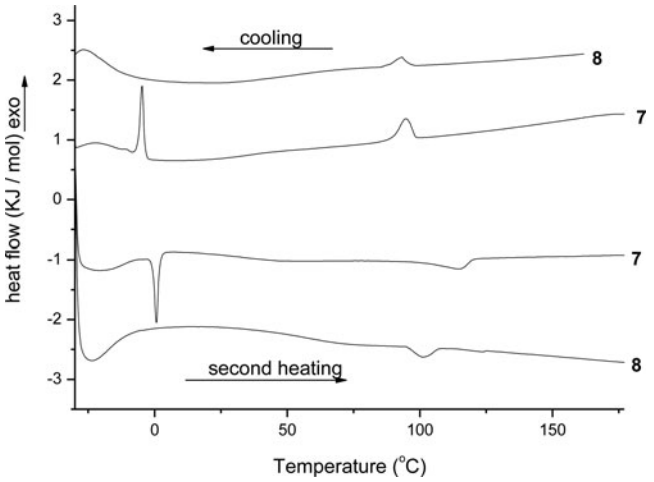


Figure 1. The DSC traces of componuds **7** and **8** on second heating and cooling (scan rate 10°C min^{-1}).

Furthermore, the mesomorphic behaviors of compounds **7** and **8** were investigated by X-ray diffraction. The XRD traces on cooling for their mesophase were illustrated in Fig. 3. One can see that both compounds **7** and **8** exhibited the strong peaks at $2\theta = 2.2°$, and 18°∼28° approximately. Compounds **7** and **8** also showed a weak peak at about 27°, respectively. These reflections data were in accordance with the column liquid crystals. The peaks at $2\theta = 2.24°$ and 2.03° indicated the distances of 39.41 Å and 43.48 Å, which agreed approximately with the

Table 1. Transition temperatures (peak temperature/°C) and associated enthalpy changes (kJ/mol in parentheses) of compounds **7** and **8**.

Compounds	Phase transition	T(ΔH) Heating scan	T(ΔH) Cooling scan
7	Cr-LC(LC-Cr)	0.4(8.8)	–5.1(8.6)
	LC-Iso(Iso-LC)	115.7(6.9)	94.5(7.2)
8	Cr-LC(LC-Cr)	–23.3(18.5)	–26.3(15.4)
	LC-Iso(Iso-LC)	101.3(4.2)	93.1(3.8)

Note. Cr = crystalline, LC = liquid crystalline, Iso = isotropic.

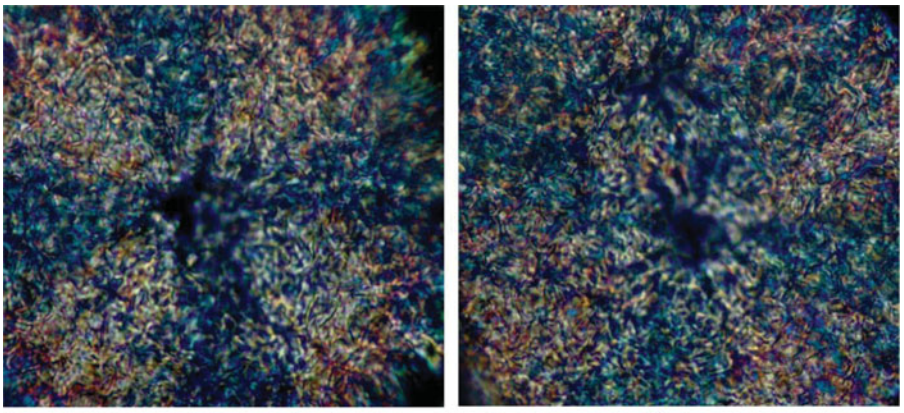


Figure 2. Textures of compounds **7** and **8** obtained with polarized optical microscopy (×400) on cooling at 80°C.

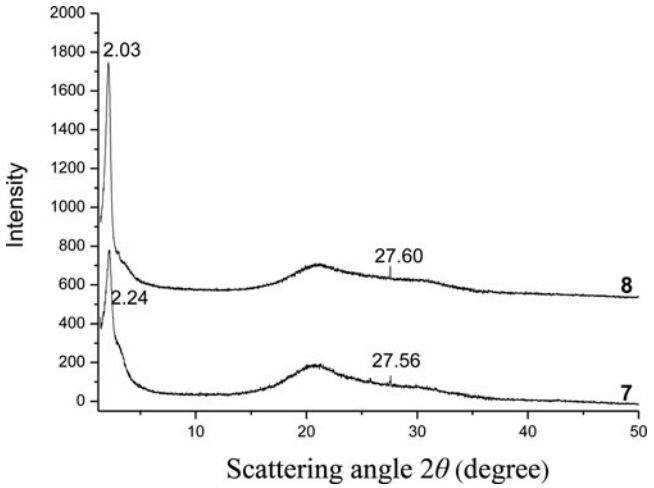


Figure 3. XRD traces on cooling for compounds **7** and **8** at 80°C.

distance of molecular unit in columns for compounds **7** and **8**, respectively. The reflections at $2\theta = 18°\sim28°$ (3.18 Å~4.92 Å broad halo) and 27° (3.30 Å) were assigned to the average distance of the molten alkyl chains and the intracolumnar order, respectively. Thus it could be deduced that compounds **7** and **8** possessed columnar liquid crystals at corresponding temperatures. But it was difficult to speculate the specific columnar structure (such as hexagonal columnar or tetragonal columnar) due to the absence of other distinct XRD peaks, which might indicate no positional order among the columns. The proposal schematic representations of the columnar molecular arrangement of compound **8** as representation were given in Fig. 4. Combining the results of DSC, POM, and XRD experiments, it could be concluded that both trimer **7** and tetramer **8** possess good room-temperature columnar mesomorphic properties. The ranges of mesomorphic temperatures for compounds **7** and **8** are as wide as 115°C and 124°C, respectively. The more gallic units are favorable for the mesomorphic properties.

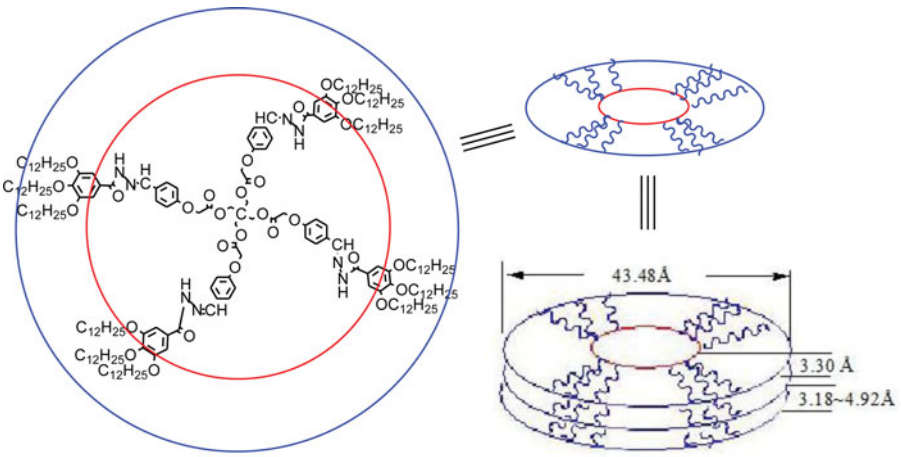


Figure 4. Schematic representations of the columnar molecular arrangements of compound **8**.

Conclusions

In conclusion, novel gallic trimer **7** and tetramer **8** based on acylhydrazone structures were designed and synthesized in yields 76% and 81%, respectively. Their structures were well characterized by elemental analysis, ESI-MS, and ^{1}H NMR spectra. Their mesomorphic studies implied that they possessed good room-temperature columnar liquid crystalline property with wide range of mesomorphic temperatures. The mesophase temperatures were 0.4∼115.7°C for compound **7** and –23.3∼101.3°C for compound **8**. The ranges of mesomorphic temperatures for compounds **7** and **8** were as wide as 115°C and 124°C, respectively. The tetramer **8** showed wider range of mesomorphic temperature and lower temperature of mesophase than that of trimer **7**, which suggested that more gallic units were favorable for the mesomorphic properties.

Experimental

All chemical reagents were obtained from Aladdin Co., Ltd. and used without further purification. The organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument at 30°C. Chemical shifts were reported in ppm, using tetramethylsilane (TMS) as internal standard. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. A polarized optical microscopy (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using a differential scanning calorimeter (DSC) (Thermal Analysis Q100) at a scanning rate of 10°C/min under N_2 atmosphere. X-ray diffraction (XRD) experiments were performed on SEIFERT-FPM (XRD7), using Cu Kα 1.5406 Å as the radiation source with 40 kV, 30 mA power. Compound **2** was synthesized according to previous literature [18].

Procedure for synthesis of compounds 5 and 6

Under N_2 atmosphere, the mixture of trimethylolpropane (or pentaerythrotol) (3 mmol) with chloroacetyl chloride (18 mmol) was stirred and refluxed for 5 hr in 20 mL of dry CH_2Cl_2. The TLC detection indicated that only one new dot appeared. The solution was washed by 3 × 20 mL distilled water and the organic layer was dried by $MgSO_4$. After evaporating solvent under reduced pressure, the viscous products of compounds **3** and **4** were obtained. They are used to prepare compounds **5** and **6** directly. The mixture of the obtained compound **3** (or **4**), *p*-hydroxybenzaldehyde (9 or 12 mmol), K_2CO_3 (15 mmol), and KI (1 mmol) was stirred and refluxed for 24 hr in 100 mL of dry MeCN under N_2 atmosphere. The TLC detection indicated that only one main dot was produced. After cooling, 100 mL of HCl solution (1 M) and 100 mL of $CHCl_3$ was added in. Then the organic layer was partitioned, dried by anhydrous $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure. The residue was treated by 20 mL of methanol to afford precipitate in refrigeratory. The precipitate was filtered and recrystallized in $CHCl_3$/MeOH. After vacuum dryness, compounds **5** and **6** were obtained as soft white solid in yields of 80% and 85%, respectively.

Compound **5**: ^{1}HNMR (400 MHz, $CDCl_3$): δ(ppm) 0.96 (t, $J = 6.4$ Hz, 3H, CH_3), 1.26 (m, 2H, CH_2), 3.99 (s, 6H, OCH_2), 4.66 (s, 6H, OCH_2CO), 6.78 (d, $J = 8.8$ Hz, 6H, ArH), 7.56

(d, $J = 8.8$ Hz, 6H, ArH), 9.48 (s, 3H, CHO). MS(m/z) (%): 620.21(M^+, 100); calculated MS m/z 620.19.

Compound **6**: ^{1}HNMR (400 MHz, $CDCl_3$): δ(ppm) 3.96 (s, 8H, OCH_2), 4.69 (s, 8H, OCH_2CO), 6.72 (d, $J = 8.4$ Hz, 8H, ArH), 7.51 (d, $J = 8.4$ Hz, 8H, ArH), 9.26 (s, 4H, CHO). MS(m/z) (%): 784.18(M^+, 100); calculated MS m/z 784.20.

Procedure for synthesis of gallic trimer 7 and tetramer 8

Under N_2 atmosphere, the mixture of compound **2** (0.35 g, 0.5 mmol) with compound **5** (1.6 mmol) or **6** (2.1 mmol) was stirred and refluxed in 30 mL of 95% EtOH overnight. TLC detection indicated the disappearance of original materials. Then the most EtOH was distilled under reduced pressure. The residue was treated by 10 mL of methanol to afford precipitate. The precipitate was filtered and recrystallized in $CHCl_3$/MeOH. After vacuum dryness, compounds **7** and **8** were obtained as white solid in yields of 76% and 81%, respectively.

Compound **7**: ^{1}HNMR (400 MHz, $CDCl_3$): δ(ppm) 0.96 (t, $J = 6.0$ Hz, 30H, CH_3), 1.22∼1.92 (m, 182H, CH_2), 3.80–4.15 (m, 24H, CCH_2O), 4.61 (bs, 6H, OCH_2CO), 6.73–7.66 (m, 18H, ArH), 8.33 (s, 3H, N = CH), 9.11 (s, 3H, NHCO). MS(m/z) (%): 2633.21 (M^+, 100); calculated MS m/z 2633.00. Anal. Calcd for $C_{162}H_{266}N_6O_{21}$: C 73.87, H 10.18, N 3.19; found: C 73.81, H 10.29, N 3.11.

Compound **8**: ^{1}HNMR (400 MHz, $CDCl_3$): δ(ppm) 0.97 (t, $J = 6.0$ Hz, 36H, CH_3), 1.23∼1.91 (m, 240H, CH_2), 3.85–4.09 (m, 32H, OCH_2), 4.58 (bs, 8H, OCH_2CO), 6.65 (d, $J = 9.2$ Hz, 8H, ArH), 6.99 (s, 8H, ArH), 7.42 (d, $J = 9.2$ Hz, 8H, ArH), 8.44 (s, 4H, N = CH), 9.01 (s, 4H, NHCO). MS(m/z) (%): 3468.42(M^+, 100); calculated MS m/z 3468.61. Anal. Calcd for $C_{213}H_{348}N_8O_{28}$: C 73.75, H 10.11, N 3.23; found: C 73.69, H 10.15, N 3.21.

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