Synthesis and Properties of Cholesteryl 4-(Alkanoylamino)benzoates: Liquid Crystals and Organogelators

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Abstract: As a new liquid crystal and organogelator, cholesteryl 4-(alkanoylamino)benzoates were prepared. Cholesteryl 4-(alkanoylamino)benzoates had enantiotropic cholesteric and chiral smectic C phases. Furthermore cholesteryl 4-(alkanoylamino)benzoates gelled organic liquid such as 1-decanol, linalool, geraniol, nerol, citronellol, linalyl acetate, lavender oil, orange oil, and rose oil. The terpene and perfume gels show good release characteristics of the volatile components for a long period.

Key words: liquid crystals, organogelators, chiral smectic C phase, cholesteric phase, terpenes

1 INTRODUCTION

Self-assembled systems are of great importance, particularly for their potential application to nanomaterials such as liquid crystals and gelators¹⁻⁴. Many studies have been reported on their structure and mechanism of molecular aggregation. More than 110,000 liquid crystalline compounds are reported till now⁵. To design a liquid crystal molecule with mesomorphic properties, a rigid core and flexible alkyl side chains are required⁶. The number of organogelators has rapidly increased over the last 20 years¹⁻³. In the past, new organogelators were often discovered accidentally, and the studies were dedicated to understanding the relationship between the structure of a gelator and its gelation behavior. The aggregation of organogelators into fibrous networks is driven by multiple weak interactions such as dipole-dipole, van der Waals, hydrogen-bonding, and π -stacking interactions. Gelators are commonly classified by their driving force for molecular aggregation: nonhydrogen-bond-based and hydrogen-bond-based gelators. Amide compounds (such as amino acid and urea) and hydroxy compounds (such as 12-hydroxystearic acid and sugars) are hydrogen-bond-based gelators, whereas anthracene, cholesterol, and tropone derivatives are nonhydrogen-bond-based gelators. Recently, we have reported several liquid crystalline organogelators called "organogelling Liquid Crystal (LC)"⁷⁻¹⁰. Several organogelling LCs,

octa-alkoxy-substituted α -diketonato copper complex¹¹, octa(dodecyl)tetrapyrrozinoporphyrazine¹², 3,4,5-trialkoxymethylamines¹³, 2-(3,4,5-trialkoxymethylamino)-5-cyanotropones¹⁴, 2,2'-di(3,4,5-trialkoxymethylamino)-5,5'-bitropones⁹, cholesteryl 4-alkoxybenzoates (2)⁷, cholesteryl alkanates, 4-cyanophenyl 4-*n*-alkoxybenzoates, 4-cyano-4'-alkoxybiphenyls, 4,4'-dialkanoyloxybiphenyls, azoxybenzene derivatives, and 2,3,6,7,10,11-hexaalkoxytriphenylenes¹⁰ and so on have been reported. Compounds (2) exhibit enantiotropic cholesteric and smectic A phases and gelled organic solvents such as 1-decanol and *n*-hexadecane. However, 2 could not be used for gel preparation at low concentration. In this paper, we report the mesomorphic and gelation properties of cholesteryl 4-(alkanoylamino)benzoates (1) as the new organogelling LCs with a cholesteryl benzoate and hydrogen-bonding groups and its application to terpene and perfume gels.

2 EXPERIMENTAL PROCEDURES

2.1 Analysis

The elemental analyses were performed at the elemental analysis laboratory of Kyushu University, Japan. The melting points were obtained using a Yanagimoto micro-melting-point apparatus. The NMR spectra were recorded

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Fig. 1 Chemical structures of **1** and **2**.

using a JEOL GSX-270 spectrometer and in CDCl_3 solutions at room temperature; the chemical shifts are expressed in δ (ppm). The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 6200) and the mesomorphic phases were observed using polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). The X-ray diffraction (XRD) measurements were carried out using a Rigaku Rint 2100 system with Ni-filtered $\text{Cu-K}\alpha$ radiation at various temperatures. The measuring temperatures were controlled using a Linkam HFS-91 hot stage.

2.2 Synthesis of **1**

A mixture of 4-(hexanoylamino)benzoic acid (0.199 g, 0.799 mmol), cholesterol (0.508 g, 1.31 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC $\cdot$ HCl) (0.175 g, 0.914 mmol), and 4-dimethylaminopyridine (DMAP) (0.139 g, 1.14 mmol) in THF (10 mL) was stirred at room temperature for 12 h. The mixture was poured into water, and the organic substance was extracted with chloroform. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was chromatographed on a silica-gel column using chloroform as the eluent to afford crystals, which were recrystallized with hexane/ethyl acetate (1:2 v/v) to afford **1_6** as colorless crystals (0.219 g, 44% yield).

1_6 (44%). ^1H NMR (270 MHz, CDCl_3) δ = 0.70 (3H, s), 0.87 (3H, d, J = 6.6 Hz), 0.88 (3H, d, J = 6.6 Hz), 0.94 (3H, d, J = 6.3 Hz), 1.08 (3H, s), 0.87–2.02 (37H, m), 2.39 (2H, t, J = 7.6 Hz), 2.47 (2H, d, J = 7.9 Hz), 4.85 (1H, m), 5.43 (1H, d, J = 4.6 Hz), 7.25 (1H, s), 7.60 (2H, d, J = 8.8 Hz), and 8.01 (2H, d, J = 8.8 Hz). IR (KBr) ν : 1467, 1537, 1601, 1680, 1713, 28, 2934, 3339 cm^{-1} . Found: C, 79.54; H, 10.24; N, 2.34%. Calcd for $\text{C}_{41}\text{H}_{63}\text{NO}_3$: C, 79.69; H, 10.28; N, 2.27%.

1_8 (30%). ^1H NMR (270 MHz, CDCl_3) δ = 0.69 (3H, s), 0.86 (3H, d, J = 6.9 Hz), 0.87 (3H, d, J = 6.9 Hz), 0.92 (3H, d, J = 6.6 Hz), 1.06 (3H, s), 0.85–2.04 (41H, m), 2.38 (2H, t, J = 7.6 Hz), 2.45 (2H, d, J = 7.6 Hz), 4.83 (1H, m), 5.41 (1H, d, J = 4.0 Hz), 7.29 (1H, s), 7.59 (2H, d, J = 8.9 Hz) and 8.00 (2H, d, J = 8.9 Hz). Found: C, 79.90; H, 10.50; N, 2.17%. Calcd for $\text{C}_{43}\text{H}_{67}\text{NO}_3$: C, 79.95; H, 10.45; N, 2.17%.

1_10 (37%). ^1H NMR (270 MHz, CDCl_3) δ = 0.69 (3H, s), 0.86 (3H, d, J = 6.6 Hz), 0.87 (3H, d, J = 6.4 Hz), 0.92 (3H, d, J = 6.3 Hz), 1.06 (3H, s), 0.85–2.04 (45H, m), 2.38 (2H, t, J = 7.3 Hz), 2.45 (2H, d, J = 7.6 Hz), 4.83 (1H, m), 5.41 (1H, d,

J = 4.6 Hz), 7.30 (1H, s), 7.59 (2H, d, J = 8.6 Hz), and 8.00 (2H, d, J = 8.6 Hz). Found: C, 79.32; H, 10.59; N, 2.06%. Calcd for $\text{C}_{45}\text{H}_{71}\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$: C, 79.13; H, 10.62; N, 2.08%.

1_12 (24%). ^1H NMR (270 MHz, CDCl_3) δ = 0.69 (3H, s), 0.86 (6H, d, J = 6.9 Hz), 0.92 (3H, d, J = 6.6 Hz), 1.07 (3H, s), 0.85–2.05 (49H, m), 2.38 (2H, t, J = 7.3 Hz), 2.45 (2H, d, J = 7.6 Hz), 4.83 (1H, m), 5.41 (1H, d, J = 4.9 Hz), 7.23 (1H, s), 7.59 (2H, d, J = 8.6 Hz), and 8.00 (2H, d, J = 8.6 Hz). Found: C, 79.35; H, 10.64; N, 1.95%. Calcd for $\text{C}_{47}\text{H}_{75}\text{NO}_3$: C, 79.30; H, 10.77; N, 1.97%.

1_14 (61%). ^1H NMR (270 MHz, CDCl_3) δ = 0.69 (3H, s), 0.88 (3H, d, J = 6.6 Hz), 0.89 (3H, d, J = 6.6 Hz), 0.94 (3H, d, J = 6.3 Hz), 1.06 (3H, s), 0.86–2.04 (53H, m), 2.39 (2H, t, J = 7.6 Hz), 2.47 (2H, d, J = 7.9 Hz), 4.85 (1H, m), 5.43 (1H, d, J = 4.6 Hz), 7.25 (1H, s), 7.60 (2H, d, J = 8.7 Hz), and 8.01 (2H, d, J = 8.7 Hz). Found: C, 80.29; H, 10.83; N, 1.99%. Calcd for $\text{C}_{47}\text{H}_{75}\text{NO}_3$: C, 80.60; H, 10.91; N, 1.92%.

2.3 Gelation of Organic Liquids with **1**

Compound **1** (100 mg) was weighed accurately into a screw cap vial. An organic liquid (1.0 mL) (*n*-hexane, *n*-decane, *n*-hexadecane, methanol, ethanol, 1-decanol, ethyl acetate, acetonitrile, or tetrahydrofuran) was added. The screw cap of the vial was closed and heated at 120°C until a clear solution was obtained. The vial was left at 25°C in an incubator for 1 h. The gelation was considered successful when upon inversion no fluid runs down the walls of the vial.

2.4 Preparation of Terpene and Perfume Gels and Release Test of Volatile Components

Cholesteryl 4-(tetradecanoylamino)benzoate (**1_14**) (30.1–32.7 mg) was weighed into a screw cap vial. Terpene (1.0 mL) (linalool, geraniol, nerol, citronellol, or linalyl acetate) or an essential oil (lavender oil, orange oil, or rose oil) was added. The screw cap of the vial was closed and heated at 120°C until a clear solution was obtained. The vial was left at 25°C in an incubator for 1 h. The release tests of the volatile components from **1_14**-linalool, lavender oil, orange oil, and rose oil gels were conducted. The caps of the glass tubes containing the fragrance gel were opened. They were left at room temperature (temperature range: 13.2–29.3°C, average temperature: 22.6°C) and their weights were measured after 50, 100, and 200 days.

3 RESULTS AND DISCUSSION

3.1 Synthesis of **1**

Compounds **1** were prepared by the esterification of cholesterol with the corresponding 4-(alkanoylamino) benzoic acid in the presence of EDC $\cdot$ HCl and DMAP. The structures and purities of **1** were established by the NMR spectral and elemental analyses.

Scheme 1

3.2 Mesomorphic Properties

The transition temperatures and thermal behaviors of the **1** were determined using a differential scanning calorimeter, a polarizing microscope equipped with a hot stage, and an XRD study. The optical micrographs of cholesteric (N^*) of **1**₁₂ and chiral smectic C (SmC^*) phases of **1**₁₄ are shown in Fig. 2. Chiral smectic C and cholesteric phases were determined from a following observation and XRD study, i.e., broken focal-conic fan, banded focal-conic fan, and schlieren textures for chiral smectic C phase¹⁵;

Fig. 2 Optical cross-polarizing micrographs of **1**₁₄ at (a) 180°C (SmC^*) and (b) **1**₁₂ at 230°C (N^*). All pictures taken on cooling from the isotropic phase.

fingerprint texture, Grandjean steps at the border and oily streak textures for the cholesteric phase. The thermal behaviors of the cholesteryl benzoates (**1** and **2**) are summarized in Table 1. Compounds **1** had a phase sequence of $\text{Cr-SmC}^* \cdot N^* \cdot \text{Iso}$, whereas **2** had a phase sequence of $\text{Cr-SmA} \cdot N^* \cdot \text{Iso}$. The melting and clearing points of **1** were higher than those of the corresponding derivatives **2**, showing that the hydrogen bonds of the amide group strengthen the intermolecular interactions.

We measured the XRD pattern of the mesophases. The smectic layer spacings (d) and molecular lengths (l) of **1** are listed in Table 2. The molecular lengths (l) of **1** were calculated by the MM2 method. The d/l ratios of chiral smectic C (SmC^*) phase of **1** are within the range 0.71–0.77, showing that the molecular long axes of **1** are tilted with respect to the normal to the layer in the SmC^* phase and form the layer as shown in Fig. 3.

3.3 Gelation Properties

We carried out the gelation test of **1** in various organic solvents (n -hexane, n -decane, n -hexadecane, methanol, ethanol, 1-decanol, ethyl acetate, acetonitrile, and tetrahydrofuran). The result of gelation test with **1** is shown in Table 3. Compounds **1** could not gel n -hexane, n -decane,

Table 1 Transition temperatures (°C) of **1** and **2**.

	Transition Temperatures/°C	
	1	2
1 ₆ (n=6)	$\text{Cr} \cdot 195.9 \cdot N^* \cdot 252.9 \cdot \text{Iso}$	$\text{Cr}_1 \cdot 113.5 \cdot \text{Cr}_2 \cdot 150.9 \cdot N^* \cdot 229.9 \cdot \text{Iso}$
1 ₈ (n=8)	$\text{Cr}_1 \cdot 109.8 \cdot \text{Cr}_2 \cdot 209.1 \cdot \text{SmC}^* \cdot 226.7 \cdot N^* \cdot 249.6 \cdot \text{Iso}$	
1 ₁₀ (n=10)	$\text{Cr} \cdot 203.3 \cdot \text{SmC}^* \cdot 223.2 \cdot N^* \cdot 242.7 \cdot \text{Iso}$	$\text{Cr} \cdot 110.4 \cdot \text{SmA} \cdot 177.7 \cdot N^* \cdot 208.1 \cdot \text{Iso}$
1 ₁₂ (n=12)	$\text{Cr}_1 \cdot 170.4 \cdot \text{Cr}_2 \cdot 175.5 \cdot \text{SmC}^* \cdot 228.8 \cdot N^* \cdot 235.8 \cdot \text{Iso}$	
1 ₁₄ (n=14)	$\text{Cr} \cdot 138.3 \cdot \text{SmC}^* \cdot 191.8 \cdot N^* \cdot 215.0 \cdot \text{Iso}$	$\text{Cr} \cdot 117.6 \cdot \text{SmA} \cdot 175.9 \cdot N^* \cdot 190.2 \cdot \text{Iso}$

Table 2 Layer spacings (Å), molecular lengths (Å), d/l values, and tilt angles (°) of **1**.

Compounds	X-Ray Diffraction		Molecular Lengths (l) /Å	d/l	Tilt Angle/°
	Temp./°C	Layer Spacings (d)/Å			
1 ₁₀	215	29.3	37.8	0.77	40
1 ₁₂	200	30.4	40.3	0.75	42
1 ₁₄	180	30.6	42.9	0.71	45

Fig. 3 Packing model of **1_14** in the smectic C* phase.

n-hexadecane, methanol, ethanol, ethyl acetate, acetonitrile, and tetrahydrofuran. Interestingly, **1** showed high gelling selectivity for 1-decanol, while **2** gelled 1-decanol and *n*-hexadecane. **Figure 3** shows the photograph of **1_14**-decanol gel and an optical micrograph of the gel phase of **1_14** in 1-decanol (5.0 w/v%) recorded at 25°C on cooling from an isotropic liquid state. Highly intertwined, rod-like fibers aligned to form the network structures by making bundles with diameters of ca. 0.8–2.0 μm. The minimum gel concentrations (MGC, g/L) of **1** and **2** are 32 for **1_6**, 27 for **1_8**, 42 for **1_10**, 31 for **1_12**, 24 for **1_14**, 33 for **2_6**, 56 for **2_10**, and 62 for **2_14**. The gelation ability of **1_14** for 1-decanol is superior than that of the other cholesteryl benzoates.

To investigate the hydrogen bonding in the gels, the IR

Fig. 4 (a) Photograph and (b) micrograph of **1_14**-1-decanol gel.

spectra of crystalline, 1-decanol gel (5.0 w/v%), and the chloroform solution of **1_14** were measured. The absorption band at 1679 cm⁻¹ of **1_14**-decanol gel was lower than that (1685 cm⁻¹) of the chloroform solution and close to that (1676 cm⁻¹) of the crystalline compound, showing that the intermolecular hydrogen bonds of the amide group play an important role in the crystal and gel states.

3.4 Preparation of Terpene and Perfume Gels

To study the application of organogelator **1** to new materials, the terpene and perfume gels were prepared. In perfume, fragrance and deodorant materials, hydrogelators such as carrageenan, agar, collagen, gellan gum, and gelatin have been used for gelations of water-containing terpenes, essential oils, and perfumes. Therefore, the purity of the oils in the gels is low and most of the components of these materials comprise water. Fortunately, under the gel-organic liquid conditions (30.1–32.7 mg/1.0 mL), **1_14** could gel the terpenoids such as linalool, geraniol, nerol, citronellol, linalyl acetate and essential oils such as lavender oil, orange oil, rose oil (**Fig. 5**).

Table 3 Gelation Ability of **1**.

	1_6	1_8	1_10	1_12	1_14
Hexane	^d Insol	^d Insol	^c Cryst	^c Cryst	^c Cryst
<i>n</i> -Decane	^d Insol	^d Insol	^c Cryst	^c Cryst	^c Cryst
<i>n</i> -Hexadecane	^d Insol	^d Insol	^c Cryst	^c Cryst	^c Cryst
Methanol	^c Cryst	^c Cryst	^c Cryst	^c Cryst	^c Cryst
Ethanol	^c Cryst	^c Cryst	^c Cryst	^c Cryst	^c Cryst
1-Decanol	^a Gel	^a Gel	^a Gel	^a Gel	^a Gel
Ethyl acetate	^c Cryst	^c Cryst	^c Cryst	^c Cryst	^c Cryst
Acetonitrile	^d Insol	^d Insol	^d Insol	^d Insol	^c Cryst
Tetrahydrofuran	^b Sol	^b Sol	^b Sol	^b Sol	^b Sol

^aGel: Gelation, ^bSol: Solution, ^cCryst: Crystallization, ^dInsol: Insoluble.

Fig. 5 Photograph of (a) **1_14**•linalool, (b) **1_14**•geraniol, (c) **1_14**•nerol, (d) **1_14**•citronellol, (e) **1_14**•linalyl acetate, (f) **1_14** • lavender oil, (g) **1_14**•orange oil, and (h) **1_14**•rose oil gels.

The release tests of the volatile components from **1_14**-linalool, lavender oil, orange oil, and rose oil gels were carried out. The results are shown in **Table 4**. The weights of the gels and neat liquids decreased with time. The rate of decrease in the weight of the gels were slower than those of the neat liquids, showing that the gel state controlled the release of the volatile components. After 200 days, each gel maintained the gel state with a characteristic scent of terpenoids and essential oil.

4 CONCLUSION

Compounds (**1_14**) exhibited mesomorphic and organogelation properties with a good gelation ability for terpenes and essential oils. We succeeded in preparing perfume gels containing 96% or more of terpene and essential oil; the perfume gels showed good release characteristics of the volatile components for a long period. The gels may be utilized as fragrance and deodorant agents.

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Table 4 Weight changes (mg) of the perfume gels containing **1_14** by release tests of the volatile components.

Solvents/Status	1_14 (mg)	Weight (mg)			
		0	after 50d	after 100d	after 200d
Linallol/Gel	30.1	877.2	838.4	811.4	732.4
Linallol/Liquid	0	877.3	832.5	801.0	713.8
Lavender Oil/Gel	32.7	962.5	922.1	899.9	850.7
Lavender Oil/Liquid	0	963.0	909.1	877.5	803.6
Rose Oil/Gel	30.6	942.9	929.6	924.6	901.4
Rose Oil/Liquid	0	943.7	914.6	906.9	884.7
Orange Oil/Gel	30.8	852.6	418.4	212.9	195.8
Orange Oil/Liquid	0	853.1	397.3	144.1	117.9

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