

Synthesis and Gelation Properties of *N,N'*-Bis(3,4,5-trialkoxy)benzoylurea: Terpene and Perfume Gels

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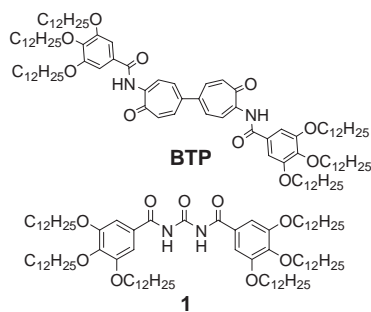
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New organogelator, *N,N'*-bis(3,4,5-tridodecyloxy)benzoylurea (**1**), gelled organic liquid such as alcohol, hydrocarbons, ethyl acetate, salad oil, terpenes, and essential and perfume oil at low concentration of gelator. The terpene and perfume gels show good release of the volatile components for a long time.

Organogels are of great significance particularly for their potential application to template for materials synthesis, drug delivery, separations, cosmetics, sensors, and biomimetics, etc.^{1,2} The number of organogelators has rapidly increased over 15 years. In the past, new organogelators often have been discovered accidentally and their studies have been dedicated to understanding the relation between the structure of gelators and gelation behaviors. 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 generally classified by their driving force for molecular aggregations into two categories of non-hydrogen bond-based and hydrogen bond-based gelators.² Amide compounds, such as amino acid³ and urea,⁴ hydroxyl compounds such as 12-hydroxystearic acid (**12-HOSA**)⁵ and sugars⁶ belong to hydrogen bond-based gelators. While cholesterol,⁷ anthracene,⁸ and tropone derivatives^{9,10} belong to non-hydrogen bond-based gelators. Recently, we have reported a new organogelator¹⁰ with a bitropone core and two 3,4,5-tridodecyloxybenzoylamino groups. The bitropone derivative (**BTP**) gelled organic liquids such as long-chain alcohol, hydrocarbon, ethyl acetate, and citronellol and its aggregation is driven by π -stacking interactions between intermolecular bitropone rings. Based on the results of critical gelation concentration (CGC), **BTP** gelled 1-decanol selectively. However, **BTP** cannot be used in low concentration. In this paper, we report the synthesis and gelation properties of *N,N'*-bis(3,4,5-tridodecyloxy)benzoylurea (**1**) as a new organogelator and its application to terpene and perfume gels (Scheme 1).

Reaction of urea with 3,4,5-tridodecyloxybenzoyl chloride



Scheme 1.

in a DMAP–pyridine solution afforded the diamide derivative **1**. The structure of **1** was identified by ¹H NMR, mass spectroscopy, and elemental analysis.¹¹

The gelation abilities of **1**, **BTP**, and **12-HOSA** for a range of organic solvent was examined by dissolving approximately 1–100 mg of compound in 1 mL of the desired solvent under heating. The solubility of these compounds at room temperature is very poor in most solvents. Upon cooling to 25 °C, a gel, a precipitate or a clear solution was observed, depending on the solvent. Interestingly, compound **1** gelled organic solvents such as ethyl acetate, alcohols (C4–C10), hydrocarbons (C6–C16), tetrahydrofuran, and salad oil. The photograph of **1**–1-decanol and **1**–ethyl acetate gels are shown in Figure 1a. Figure 1b shows

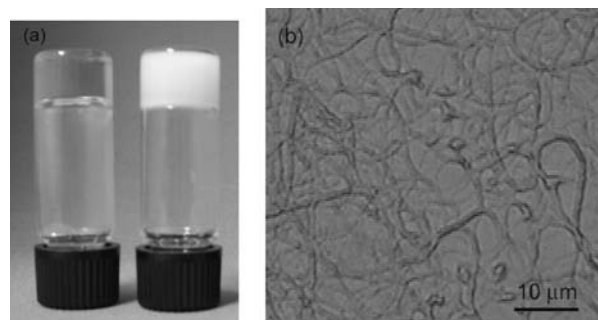


Figure 1. Photographs of (a) **1**–1-decanol gel (left, 1.0 mg/1 mL), **1**–ethyl acetate gel (right, 10 mg/mL) and (b) optical micrograph of **1**–ethyl acetate gel (10 mg/1 mL).

Table 1. Minimum gel concentrations (MGC, g L⁻¹) of **1**, **BTP**, and **12-HOSA** at 25 °C

Solvents	1	BTP	12-HOSA (80%)	12-HOSA (99%)
Salad Oil	1.9	7.4	21	2.2
<i>n</i> -Hexane	8.4	Sol ^b	30	6.5
<i>n</i> -Decane	3.5	70	20	2.8
<i>n</i> -Hexadecane	3.3	9.1	8.6	1.9
Methanol	Cryst ^a	Insol ^c	Sol ^b	Sol ^b
Ethanol	Cryst ^a	Insol ^c	Sol ^b	Sol ^b
1-Propanol	20	Insol ^c	Sol ^b	Sol ^b
1-Butanol	2.5	Insol ^c	Sol ^b	Sol ^b
1-Hexanol	1	16.5	Sol ^b	Sol ^b
1-Octanol	1	9.8	Sol ^b	95
1-Decanol	1	5.3	Sol ^b	90
Ethylacetate	3.3	11.5	Sol ^b	45
THF	25.7	Sol ^b	Sol ^b	Sol ^b
DMF	Sol ^b	Sol ^b	Sol ^b	Sol ^b

^aCryst: Crystallization. ^bSol: Solution. ^cInsol: Insoluble.

an optical micrograph of the gel phase of **1**-ethyl acetate (5.0 wt %) taken at 25 °C on cooling from an isotropic liquid state. Highly intertwined, rod-like fibers were observed in a network structure. The fibers with diameters of ca. 1 μm align to form network structures. The XRD pattern for xerogel of **1** (prepared from **1**-ethyl acetate gel) display a single broad reflection peak at $d = 2.9$ nm in the small-angle region and one broad reflection in wide range region at $d = 0.4$ nm. However, it is unclear whether the broad band in wide-range region is based on the coexistence of different mesomorphic organizations or slightly disordered structure of the organogel.¹² The layer spacing (d) is shorter than the extended molecular length (4.4 nm) of **1**, suggesting that it forms a tilted layer or interdigitated structure.

Minimum gel concentrations (MGC, g L^{-1}) of **1**, **BTP**, and **12-HOSA** (80% from Tokyo Kasei and 99% from Aldrich) for various solvents are determined as shown in Table 1. The gelation ability of **1** is better than that of **BTP**. Compound **1** is a good organogelator for long chain alcohol. That is, **1** has a long chain alcohol gelation selectively. While **12-HOSA** has long chain hydrocarbon gelation. The MGC value of **1**, **BTP**, and **12-HOSA** decrease with increasing of carbon number in hydrocarbon and alcohol. The gelation ability of **1** for alcohol is superior to that of **12-HOSA**, while that of **1** for hydrocarbon is inferior to that of **12-HOSA**. This suggest that the solvent alcohol inhibit intermolecular hydrogen bonding between hydroxyl group and carboxylic acid of **12-HOSA**.

As an application to new materials of organogelator **1**, terpene and perfume gels were prepared. In perfume, fragrance and deodrant goods, water-soluble gelators such as carrageenan, agar, collagen, gellan gum, and gelatin, etc. have been used for the gelations of water-containing terpenes, essential oils, and perfumes. So, the purity of the oils in the gels is low and most of components of these goods are water. Fortunately, under the conditions of gel-organic liquid (1–5 mg/1 mL), compound **1** could gel the terpenoids and essential oils such linalool, geraniol, nerol, citronellol, α -terpineol, nerolidol, limonene, myrcene, β -pinene, 3-carene, terpinene, squalene, linalyl acetate, neryl acetate, citronellal, rose oil, lavender oil, bergamot oil, Japanese mint oil, terpenin oil, orange oil, and lemon oil, etc. (Figure 2). Under similar condition, **12-HOSA** could gel the terpene hydrocarbons such as myrcene, β -pinene, 3-carene, terpinene, limonene, squalene, and essential oils containing much amount of terpene hydrocarbons such as orange oil and lemon oil, but could not gel the terpene alcohols.

The release tests of the volatile components from **1**-terpene and perfume gels were employed. The caps of the glass tubes



Figure 2. Gels (5 mg/1 mL) of **1**-citronellol, **1**-rose oil, **1**-lavender oil, **12-HOSA**-limonene, **12-HOSA**-orange oil, and **12-HOSA**-lemon oil.

Table 2. Weight changes (mg) of the perfume gels containing **1** and neat liquids by the release tests of the volatile components

Solvents/Status	1 /mg	Weight /mg	Weight (mg) after 324 d
Linallol/Gel	1.865	595.8	469.8
Linallol/Liquid	0	590.0	442.1
Rose oil/Gel	1.863	607.0	569.2
Rose oil/Liquid	0	597.5	558.1
Lavender oil/Gel	1.969	670.1	607.2
Lavender oil/Liquid	0	658.3	565.8
Bergamot oil/Gel	1.919	596.9	479.9
Bergamot oil/Liquid	0	568.6	309.9

containing the fragrance gel and neat liquid were opened, they were left at room temperature, and the weight changes of the gels and neat liquids were investigated, as shown in Table 2.

The weights of the gels and neat liquids were decreasing with time. The weight-decreasing rates of the gels were slower than those of neat liquids, suggesting that the gel state controlled the release of the volatile components. After 324 d, each gel was keeping the gel state and had a characteristic scent of the terpene and perfume.

In conclusion, compound **1** had good gelation ability for terpenes and essential oils. We succeeded in preparation of the perfume gels containing 99.5% or more of terpenes and essential oil for the first time. The terpene and perfume gels showed good release of the volatile components for a long time. Their gels will be utilized as fragrance and deodorant agents.

References and Notes

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- Spectral data of **1**: ¹H NMR (400 MHz, CDCl₃) δ 0.88 (18H, t, $J = 7.0$ Hz), 1.26–1.52 (108H, m), 1.75 (4H, quint, $J = 6.6$ Hz), 1.84 (8H, quint, $J = 6.6$ Hz), 4.05 (4H, t, $J = 6.6$ Hz), 4.06 (8H, t, $J = 6.6$ Hz), 7.14 (4H, s). FAB MS: m/z 1374 (M + H). Found: C, 75.93; H, 11.38; N, 1.99%. Calcd for C₈₇H₁₅₆N₂O₉: C, 76.04; H, 11.44; N, 2.04%.
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