

Fabrication of resonance core assisted self-assembling gelators derived from cyclohexanone



Yan-Song Zhang^a, A.V. Emelyanenko^b, Jui-Hsiang Liu^{a,*}

^a Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

^b Department of Physics, Moscow State University, Moscow 119991, Russia

ARTICLE INFO

Article history:

Received 2 February 2016

Revised 13 April 2016

Accepted 6 May 2016

Available online 27 May 2016

Keywords:

Self-assembly

Chiral

Resonance

Xerogels

Asymmetric constructions

ABSTRACT

Three high-resonance core compounds, **BHC-6**, **BHC-11** and **BHC-cho**, were synthesized. The morphologies of the self-assembled xerogels of the synthesized compounds were studied using SEM and TEM. The molecular interactions and the formation of asymmetric constructions were investigated using temperature-dependent ¹H NMR spectroscopy and circular dichroism spectrometry, respectively. The induction of an asymmetric helical structure was further confirmed using TEM. The results show that increasing the resonance length strengthens intermolecular forces, leading to the formation of gels. A chiral environment produces a steric field effect, leading to the formation of asymmetric constructions. The interactions between functional groups were further confirmed using 2D nuclear overhauser effect spectroscopy NMR. The reversible E-Z isomerization and dimer formation of cinnamoyl derivatives were investigated using UV-vis and fluorescence spectrometry, relatively.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

Gels are solid, jelly-like materials formed from colloidal mixtures. Their solid-like appearance results from the dispersion and entrapment of the gelator within a liquid in a solid three-dimensional (3D) matrix with a large surface area. Gels consist of solid 3D networks formed by physical bonds (physical gels) or chemical bonds (chemical gels). Gels can be divided by composition into low-molecular-weight gelators (LMWGs) and macromolecular gelators [1–3]. LMWGs are able to form gels with various organic (organogel) and aqueous (hydrogel) solvents, demonstrating reversible properties as a result of physical entanglements based on non-covalent interactions, including H-bonding, π – π stacking, and van der Waals interactions [4]. Recently, LMWGs have attracted attention due to their potential use in supramolecular chemistry and technical applications [5–11]. Especially when equipped with functional and chiral moieties because of significant changes in their physical properties during gel formation [12–14]. Among these LMWG materials, many attempts have been made to synthesize and create novel nanostructures using hydrogen bonds. However, the design of a gelling agent without H-bonding and only relying on weak intermolecular interactions remains challenging. In these systems, the structural requirements for the molecule cannot be predicted and must be determined experimentally [15].

The reversibility of the secondary binding forces indicates that LMWGs are easily manipulated by external stimuli, such as thermal and electrochemical stimuli, and photoirradiation; this enables the physical properties of the gels to be tuned [16–20]. In this study, three thermo-tunable organogelators were synthesized *via* the reactions of various terminal groups with 2,6-bis-(4-hydroxybenzylidene) cyclohexanone (**BHC**). It is well known that **BHC** derivatives contain a long-resonance-length core exhibiting tunable fluorescence, photochromism, and liquid crystals [21]. In addition to that, in order to increase the terminal interaction between molecules, OH group was introduced at both terminals of **BHC-6** and **BHC-11** with different spacer length. To date, no examples of organogelators with **BHC** moieties have been reported. A cholesteryl group was further introduced onto **BHC** to investigate the correlation between the gelation ability and chemical structures of **BHC** and the effect of external thermal stimuli on molecular self-assembly. To investigate the molecular interactions between the gelators, temperature-dependent ¹H NMR spectroscopy and X-ray diffraction (XRD) analysis were used.

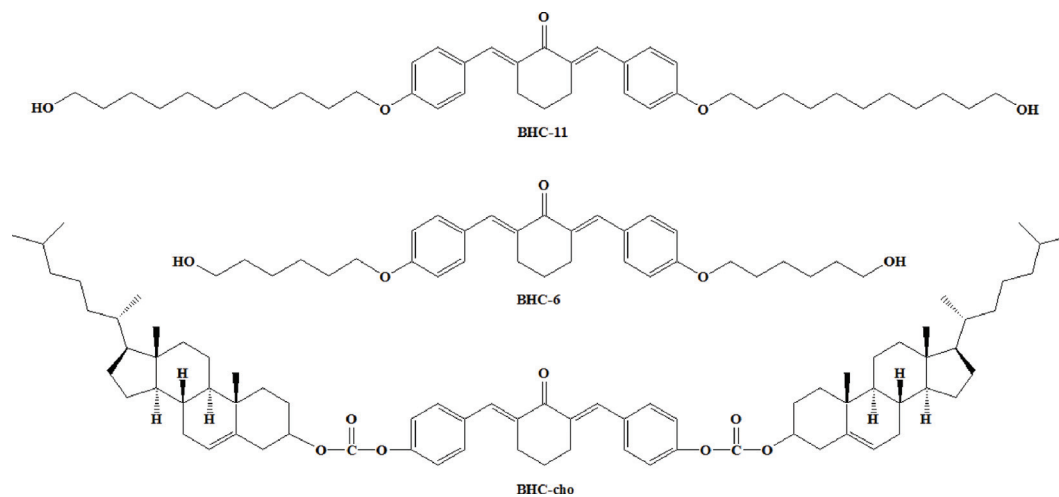
2. Experimental

2.1. Synthesis of organogelators

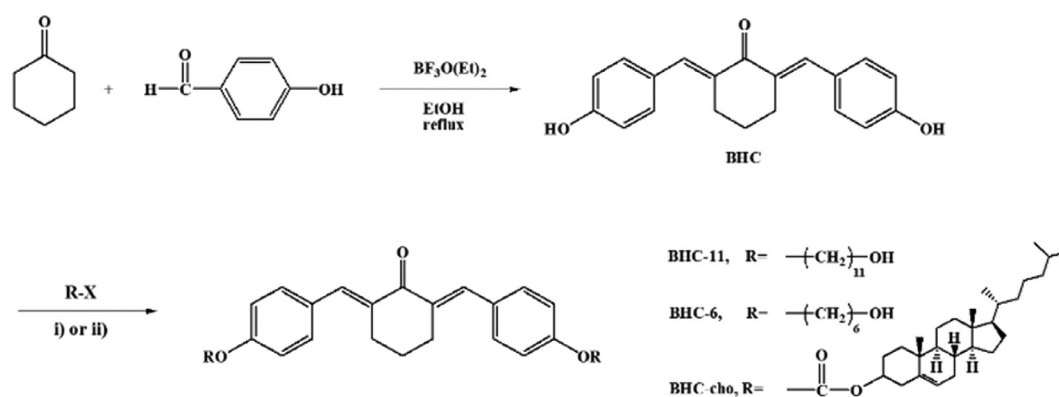
In this study, as shown in **Scheme 1**, three thermo-tunable organogelators containing cinnamoyl groups were synthesized to investigate the correlation between gelation ability and chemical structure. In each compound, a large resonance core is located

* Corresponding author. Tel.: +886 62757575; fax: +886 6 2384590.

E-mail addresses: emel@polly.phys.msu.ru (A.V. Emelyanenko), jhliu@mail.ncku.edu.tw (J.-H. Liu).



Scheme 1. Chemical structures of the gelators **BHC-11**, **BHC-6** and **BHC-cho**.



Scheme 2. Synthesis of **BHC-11**, **BHC-6** and **BHC-cho**. Reagents and conditions: (i) KOH, EtOH, reflux for **BHC-11** and **BHC-6**; (ii) Et₃N, DMAP, THF for **BHC-cho**. X = Br for **BHC-11**; X = Cl for **BHC-6** and **BHC-cho**.

in the center. The long resonance length, which included oxygen, a benzene ring, and the central cyclohexanone, promote significant interactions for the self-assembly of molecules. In addition, chiral **BHC-cho** contains chiral cholesteryl groups at its terminals. The cholesteryl group typically features a strong van der Waals force and some specific steric effects. The molecule further contains polar carbonyl groups at both sides of the resonance core. The synthetic procedures for the three compounds are shown in Scheme 2.

2.1.1. Synthesis of 2,6-bis(4-hydroxybenzylidene) cyclohexanone (**BHC**) [22]

Compound **BHC** was synthesized from cyclohexanone and 4-hydroxybenzaldehyde using boron tri fluoride diethyl etherate as a catalyst as follows. A solution of cyclohexanone (1.47 g, 15 mmol) and 4-hydroxybenzaldehyde (4.03 g, 33 mmol) in EtOH (50 ml) was stirred vigorously and heated at reflux for 1 h. Next, 10 drops of boron tri fluoride etherate (BF₃O(Et)₂) were added to the solution and heated at reflux for 24 h. After the subsequent reaction, the mixture was allowed to cool to room temperature, and the solution was condensed under reduced pressure. The mixture was then poured into water, and the precipitate was filtered and washed with distilled water for three times. **BHC** was obtained as a dark green powder after drying the product in vacuum. Yield: 49.6%.

¹H NMR (DMSO-d₆, δ in ppm): 1.68–1.71 (m, 2H, 4-CH₂), 2.84 (m, 4H, 3-CH₂ and 5-CH₂), 6.81–6.83 (d, 4H, ortho-ArH to -OH), 7.38–7.40 (d, 4H, ortho-ArH to -CH=), 7.52 (s, 2H, -CH=), and 9.91 (s, 2H, OH).

2.1.2. Synthesis of **BHC-11**

A solution of KOH (0.75 g, 13.44 mmol) in EtOH/H₂O (80/20 ml) was added at 30 °C to a solution of **BHC** (1.03 g, 3.36 mmol) and KI in EtOH (50 ml). After stirring at reflux for 1 h, a solution of 11-bromo-1-undecanol (2.11 g, 8.4 mmol) in EtOH (20 ml) was added dropwise to the solution and heated at reflux for 24 h. After the subsequent reaction, the solution was cooled to room temperature, and the precipitate was filtered. The solvent was removed under reduced pressure, poured into water, and acidified with HCl (5%) to pH 2. The precipitate was filtered, washed with water, and then dried under vacuum. The crude product was purified by recrystallization in ethanol twice. Yield: 41.3%.

FT-IR (KBr, ν_{max}/cm⁻¹): 3295 (-OH), 2917, 2850 (C-H), 1903 (C=O), 1602, 1577 (C=C), 1253, 1292 (C-O-C). ¹H NMR (CDCl₃, δ in ppm): 1.30–1.58 (m, 36H, CH₂), 1.78–1.82 (m, 2H, 4-CH₂), 2.91–2.93 (m, 4H, 3-CH₂ and 5-CH₂), 3.63–3.66 (t, 4H, ortho-CH₂ to -OH), 3.98–4.00 (t, 4H, -CH₂OPh), 6.91–6.93 (d, 4H, ortho-ArH to OCH₂-), 7.43–7.45 (d, 4H, ortho-ArH to -CH=), 7.75 (s, 2H, -CH=). Elemental analysis: calculated for C₄₂H₆₂O₅, C 77.90, H 9.58; found C 77.73, H 9.58.

2.1.3. Synthesis of **BHC-6**

Compound **BHC-6** was synthesized in a similar manner as compound **BHC-11**. Yield: 32.3%.

FT-IR (KBr, ν_{max}/cm⁻¹): 3313 (-OH), 2861, 2935 (C-H), 2028 (C=O), 1600 (C=C), 1257, 1288 (C-O-C). ¹H NMR (DMSO-d₆, δ in ppm): 1.33–1.47 (m, 16H, CH₂), 1.69–1.75 (m, 2H, 4-CH₂), 2.87–2.88 (m, 4H, 3-CH₂ and 5-CH₂), 3.38–3.41 (t, 4H, ortho-CH₂ to

Download English Version:

<https://daneshyari.com/en/article/690240>

Download Persian Version:

<https://daneshyari.com/article/690240>

[Daneshyari.com](https://daneshyari.com)