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Multi-responsive supramolecular organogel with a crystalline-like structure

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ABSTRACT

A multi-responsive cyclodextrin-based organogel with a crystalline-like structure is first reported. An amount of β-cyclodextrin (β-CD) and lithium chloride (LiCl) was added into *N*,*N*-dimethylformamide (DMF), and the system obtained could transform instantly from a transparent solution into a gel state by introducing ethylene diamine (EDA), and then the gel could turn into another precipitate-like gel by undergoing a heating–cooling process. Among a series of aliphatic amines, only EDA was found to be able to induce the gel formation. Both the gels possess crystalline-like structures in their morphology with sheet-like layers, in a highly-ordered channel-type packing mode, which were proved by OM, SEM, XRD, and FT-IR measurements. Furthermore, the gel could respond to H^+ and Cu^{2+} by transforming into an amorphous precipitate. This research may pave the way for the design of novel smart materials.

1. Introduction

Supramolecular gels based on low-molecular-weight-organogelators (LMOGs), which are mainly formed by self-aggregation of small gelator molecules to 3-D microstructure, have received increasing attention during recent years.[1–9] Basically, the intrinsic property of supramolecular gels is a phase transition from solution to gel over a macroscopic scale, with the phase transition making supramolecular gels amenable to external stimuli such as chemicals, light, electricity, and temperature.[4,10–12] This has been ascribed to the weak non-covalent bonds in the gels predominantly hydrogen bonds, van der Waals, charge-transfer, π–π stacking, and coordination interactions. Supramolecular gelators could be designed to achieve certain functions by incorporating specific units, such as pH or redox sensitive functional groups.[13] LMOGs based on CDs and their derivatives are currently arousing significant interests owing to their potential applications in analysis, drug delivery, and stabilization.[13–19] Host–guest interactions of CDs with guests were efficiently employed in constructing the supramolecular gels.[20–22] According to the property of the gelators, the transition can be either reversible or irreversible. This characteristic makes the gels highly likely to be applied in the areas of sensors, drug delivery, catalysis, memory systems, and molecular imprinting.[1–5]

Three possible molecular aggregation modes, crystallization, gelation, and amorphous precipitation, may occur when the molecules start to condense.[4] Crystallization belongs to a highly-ordered aggregation mode, while gelation can range between highly-ordered and random aggregations. In the last few decades, gels have been successfully employed as the media for the growth of inorganic and organic crystals.[23–29] However, research on the competition of gelation and crystallization during the formation of gels remains a challenge.[30–35] Constructing supramolecular gels with a structure similar to crystalline may help chemists to better understand the mechanism of the gel-formation, and to design new functional materials more effectively.[30–33] For example, Dastidar and co-workers[35] reported a gel that could transfer completely into macroscopic crystals. Tang et al.[31] succeeded in obtaining crystals from a supersaturated gelator solution. Gels and crystals are two independent phases with distinctive properties. Therefore, it is a tough task to construct a gel system which resembles either a crystal structure or a crystalline-like structure. It is believed that the combination of stimuli-responsive property and the crystalline-like structure will create more potential applications, for example, performing as a novel composite material.[25]

In this paper, we report a new kind of organogel with a crystalline-like structure, which can respond to H^+ and Cu^{2+}. Furthermore, the gel can form another precipitate-like gel after a heating-cooling process. Among a class of aliphatic amines only EDA can induce gel formation in the pre-gel system. These special properties would endow the gel to be a favorable candidate for potential functional materials.

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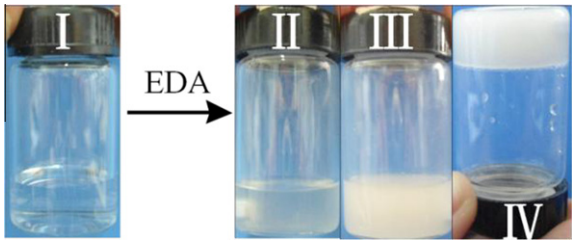

Figure 1. The gel formation process of the β-CD/LiCl/DMF system: a clear solution (I), a turbid liquid (II) after injecting EDA, a gel to be (III), gel (IV) at room temperature.

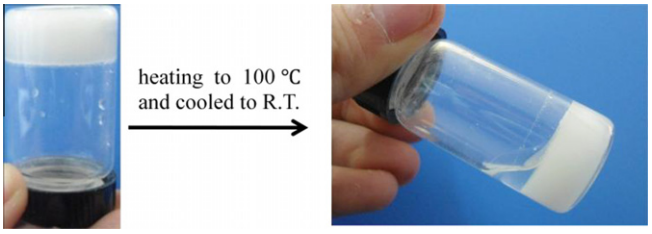

Figure 3. Images of gel and after the heating–cooling process. ($C_{\beta\text{-CD}}$ = 0.147 mol/L, C_{EDA} = 0.2 mol/L, ω_{LiCl} = 0.5%).

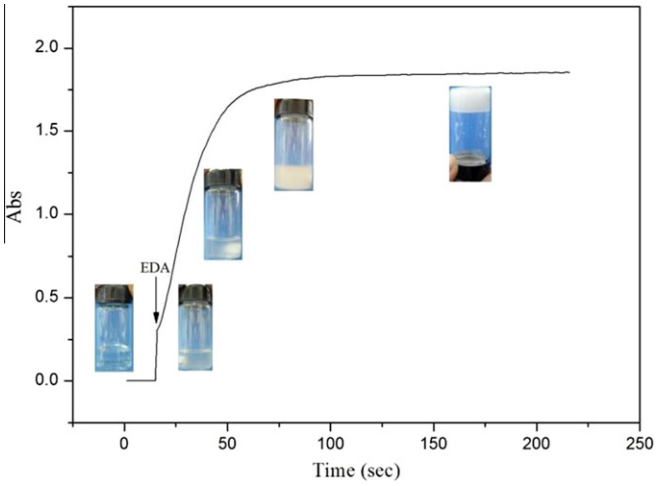

Figure 2. Visible light spectra (n = 550 nm) of sol–gel transformation process at room temperature. ($C_{\beta\text{-CD}}$ = 0.147 mol/L, C_{EDA} = 0.2 mol/L, ω_{LiCl} = 0.5%).

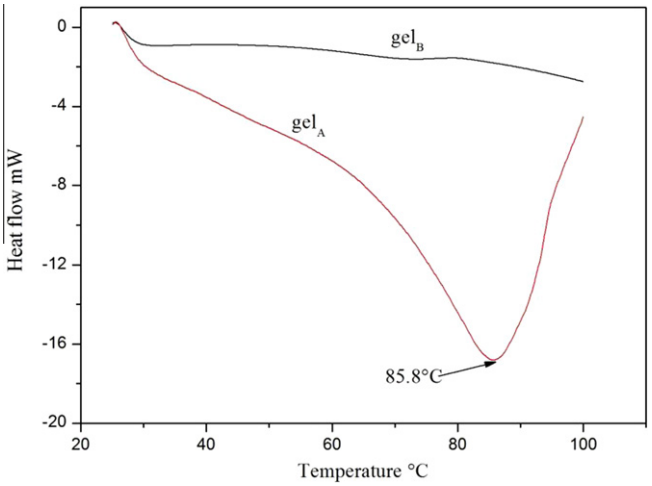

Figure 4. DSC thermograms of the gel and thermal precipitate. ($C_{\beta\text{-CD}}$ = 0.147 mol/L, C_{EDA} = 0.2 mol/L, ω_{LiCl} = 0.5%).

2. Results and discussion

2.1. Formation of the gel

First, a solution of β-CD and LiCl in DMF at room temperature was prepared. The solution quickly turned opaque upon the introduction of EDA. Then, in a few minutes, the mixture transformed into a gel. The formation process of the gel induced by EDA from a clear solution was investigated and is shown in Figures 1 and 2 by visible light absorbance at a wavelength of 550 nm (wavelength at 400, 450 nm see Fig. S1).

In Figures 1 and 2, the solution of β-CD and LiCl in DMF is clear and transparent. When EDA was injected into the solution, the solution instantly became turbid, in agreement with the abruptness of light absorbance at 15 s after a tiny disturbance. The system became more opaque with increasing light absorption. About 150 s later, the solution transformed into a white colored soft material with fluidity. The system completely turned into a gel at around 200 s, when the absorption presents a smooth and fixed curve. The gel formed in a spontaneous way, indicating that no external energy such as a stirring or cooling process was needed. EDA, β-CD and LiCl are believed to be essential constituents for the formation of the gel. The system would turn into a precipitate without LiCl or a clear solution without β-CD or EDA.

2.2. Thermal responsive properties

The influence of temperature on gel morphology was also investigated. When heated to 100 °C, the gel (gel_A) turned into a precipitate. Then the precipitate transformed into another precipitate-like gel (gel_B) when it was cooled down to room temperature (Fig. 3).

Differential Scanning Calorimeter (DSC) measurement was employed to investigate the thermal properties of the gel. As shown in Figure 4, gel_A demonstrates a clear and huge endothermic peak at 85.8 °C which corresponds to the phase change observed in the test tube approach. The endothermic peak may be attributed to the influence of the hydrogen bonds (Fig. 8) and the crystalline lattice (Fig. 5) as the temperature increased. After cooling down, the crystal structure reforms, making itself into another more stable and compact precipitate-like gel. Compared with gel_A, gel_B shows no clear thermal behavior, which is reflected by a comparatively more smooth curve of DSC. The results indicated that gel_B was formed from the precipitate, and was more stable than gel_A which formed directly from solution and EDA.

2.3. Microstructure of the gel

Cross-polarized optical images for the gel samples at different magnifications are shown in Figure 5A and B. A mass of crystal-like platelets was observed. Basically, most of the platelets are square in shape as shown in the OM images. The size of the platelets is about 10–20 μm in width and length, and they stack compactly in a disorder state. Surprisingly, some of these flakes appear colorful under cross-polarized light, indicating the formation of anisotropic particles or crystals.[23,28,37] The appearance of the crystals can be employed to explain the assembling trend of the gel. The areas of the crystals are random and only a few of them can be observed. Therefore, we are reluctant to define the gel structure as a crystalline structure. The results reveal that the gel retains a state close to a crystal, and some of the areas appear to have crystal phase behavior.

Scanning electron microscopy (SEM) is the most common and powerful test method for observing the surface micro-morphology