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Self-Assembly of Amino-Acid-Based Dendrons: Organogels and Lyotropic and Thermotropic Liquid Crystals

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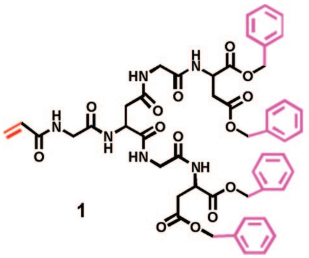
The design and synthesis of multifunctional materials with tailored properties are topics of considerable importance.[1] Multiple weak interactions as driving forces behind molecular assembly lead to numerous supramolecular architectures such as organogels and liquid crystals (LCs).[2] With molecular architectures totally different from the conventional gelators, dendritic gelators are newcomers to the field of organogels, and have renewed great attention.[3] In particular, dendritic gelators based on natural amino acids are of much interest because of their potential applications in gene therapy and drug delivery.[4] For example, lysine-based dendritic gelators have been systematically studied by Smith et al.[5] Recently, we have also synthesized the dendrons with different amino acids as building blocks and studied their dendritic architecture dependence on self-assembly.[6] Because a small change on chemical structure can make their assembly behavior significantly different,[7] an understanding of the structure–property relationships of dendrons and/or dendrimers has not yet been thoroughly surveyed.

Table 1. Gelation Behavior of 1 and 2 in Organic Solvents

solvents	1[a]	2[a]
methanol	G(6)	S
ethanol	G(7)	S
ethyl acetate	G(10)	G(22)
benzene	G(8)	G(6)
toluene	G(6)	G(10)
THF	G(4)	S
chloroform	G(5)	S
benzyl alcohol	G(22)	S
DMSO	S	S
DMF	S	S

[a] G, P, and S denote gelation, precipitation, and soluble, respectively. The critical gelation concentration (mg/mL) is shown in parentheses.

Herein, we intend to further describe how a minor chemical difference in the dendrons will impact on their self-assembly behavior. The dendritic portion based on two natural amino acids of glycine and aspartic acid were synthesized according to our previous report,[6a] and dendron **1** was further modified with an acrylic group at the focal points (see the Supporting Information). Using various characterization techniques, we found that both of the modified dendrons gelled common organic solvents, but with different structures of molecular packing. Moreover, dendron **1** also exhibits versatile properties indicative of lyotropic and thermotropic liquid crystals.



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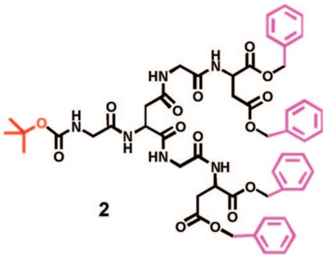

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The gel samples of **1** and **2** were prepared by using a typical method: A specific weight of gelator was dissolved in an organic liquid with heat and subsequently cooled to room temperature. If the solvent was apparently immobilized without fluid by inverting the cuvette, it was considered as gel. The interconversion of gel-to-sol and sol-to-gel was fully thermoreversible using several cycles of heating and cooling. It was found that **1** gelled many organic solvents at a very low concentration (<1 wt %). For example, 4 mg of **1** can gel 1 mL of THF, namely, one **1** molecule could entrap ~3000 THF molecules. Dendron **2**, whose focal point is capped by a Boc group, also forms gels in a few common solvents but at relative high concentrations. The solvents that can be gelled by **1** and **2** are summarized in Table 1. As

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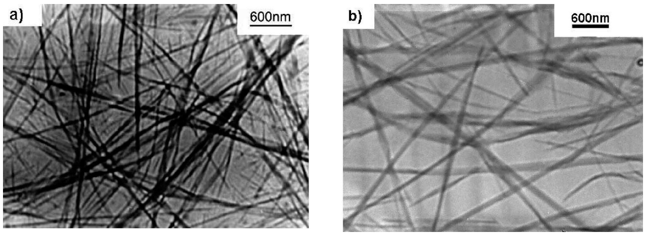

Figure 1. TEM images of xerogel made from **1** in chloroform ($c = 5$ mg/mL) (a) stained by uranyl acetate. (b) TEM image of a dried dilute gel of **2** in toluene ($c = 6$ mg/mL).

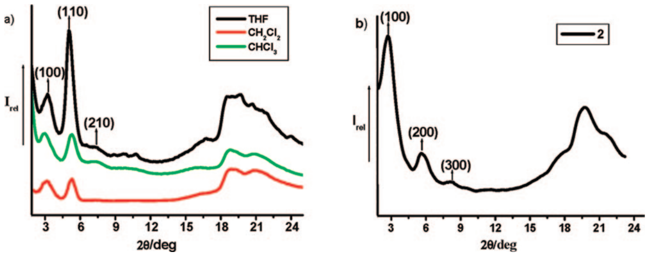

Figure 2. (a) WAXD patterns of xerogels **1** from different solvents. (b) WAXD patterns of xerogel **2** from benzene.

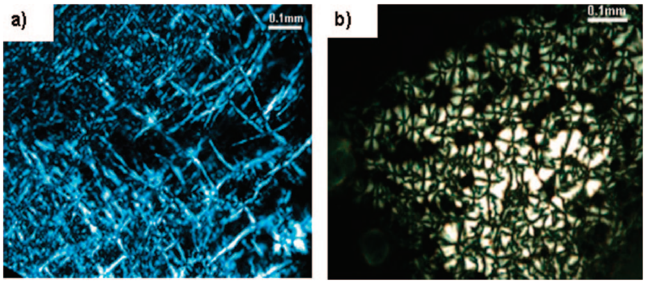

Figure 3. (a) POM image of lyotropic and (b) thermotropic LC textures of **1**. The sample of (a) contained 33 wt % **1** in benzyl alcohol and was annealed at 45 °C after cooling from the isotropic state (wet state). (b) POM image of pure **1** cooled from isotropic state to room temperature.

Table 1 shows, the structure of the dendron focal point has a huge influence on the gelation behavior. This result is consistent with that of the dendritic gelators composed of the peptidic core and Frechet-type dendrons studied by Aida et al.[7a,b]

The morphology of the xerogels (air-dried gels) of **1** and **2**, which may be a reflection of the morphology in the wet state, was examined under transmission electron microscopy (TEM). Figure 1a depicts the sample of the gel of **1** dried onto a full carbon-film covered grid and stained with uranyl acetate. Compared with that of the pristine sample, staining enhanced the image contrast and had negligible change in morphology. Similar to other dendrons,[3] the molecules of **1** self-assembled into a ramified network of intertwined fibers. The fibers are 70−90 nm in diameter and extend over several micrometers. The TEM image of the xerogel from **2** formed in toluene also reveals a similar morphology, wherein the fiber diameter (or width) presents a broad distribution from 50 to 250 nm (Figure 1b). Circular dichroism (CD) was used to explore the chiral structure of the gel phase aggregates. Significant negative Cotton effect, which did not show in solution, was observed in the gel state (Supporting Information). The λ_{max} value of the CD signal appeared at 224 nm, which could be assigned to the amide carbonyl group of the dendritic branches, implying that the gelators may self-organize in a helical way. However, the twisted fiber morphology could not be unambiguously observed in our TEM images.

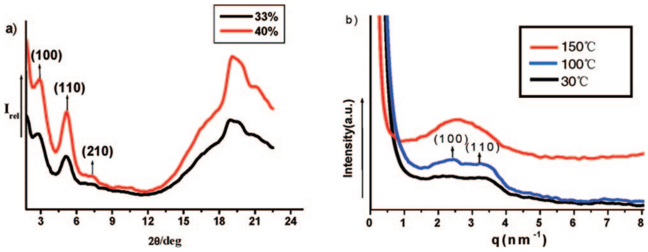

Figure 4. (a) 1D XRD patterns of **1** in benzyl alcohol at different concentrations. (b) SAXS pattern of **1** obtained at 80 °C after slow cooling from the isotropic state.

Hydrogen-bonding and aromatic ring stacking may account for the gel formation. FTIR spectra showed the characteristic amide I, II, and N−H stretching absorption bands of **1** in chloroform solution (0.1 mg/mL) at 1660, 1530, and 3448 cm^{-1}, respectively; but these bands were shifted to 1631, 1526, and 3305 cm^{-1} when the gel of **1** was formed (chloroform, 5 mg/mL), indicating the existence of amide hydrogen-bonding. However, **1** was also effective in gelating solvents that strongly competed for hydrogen-bond formation, like some alcohols, suggesting other weak interactions might exist at a certain extent. We presume that aromatic-stacking between the phenyl rings is another possible driving force responsible for gelation.[6a,b] In a pyrene probe test (Supporting Information), the relative ratio of the peak 1 ($\lambda = 379$ nm) and 3 ($\lambda = 392$ nm) of pyrene emission decreased gradually with increasing concentration of gelator, which strongly supported that there was nonpolar domain formation due to the peripheral benzyl groups.

X-ray diffraction (XRD) experiments on the xerogels were performed to elucidate the possible molecular packing patterns of the gels from **1** and **2**. The XRD patterns of xerogels of **1** prepared from different solvents show the same feature (Figure 2a). The peaks in the low-angle region follow the scattering vector ratios of $1:\sqrt{3}: \sqrt{7}$, indicating a columnar hexagonal lattice with $a = b = 3.60$ nm. In the wide-angle region, the broad halo with ca. 0.46 nm corresponds to the fluidlike nature of this phase. The small-angle X-ray scattering (SAXS) profiles of the xerogel reveal no further diffraction at the low angle area. Considering the approximate extended molecular length of **1** is 2.0 nm as obtained by MM2 method, it can be proposed that the molecules self-organize in a columnar hexagonal model similar to that reported of Percec et al.[8] The hexagonal packing of **1** has a short intercolumnar distance of 3.60 nm. However, from the powder XRD pattern of xerogel of **2** prepared in benzene, it was found that **2** self-organized in a different way. Three distinct peaks appear at $d = 3.20$, 1.58

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and 1.06 nm, which indicate lamellar packing (Figure 2b). According to our previous calculation based on CPK molecular models, the size (from the focal point to the periphery) of the Boc-functioned dendron is estimated to be about 2.2 nm if **2** is in a fully extended state. Hence, the lamellae could be a bilayer structures. each lamella might consist of two layers of **2**, in which the molecules are partially interdigitated. In the inner part of the lamellae, the **2** molecules might associate with their neighbors through hydrogen-bonds, whereas the benzyl rings of the molecules are packed on the lamellar top and bottom surfaces.[7a,b]

It is of interest to see if the amino-acid-based dendrons can exhibit LC properties. Usually, it is considered to be very difficult to find that low molecular compounds are capable of gelling solvents and displaying a thermotropic mesomorphic behavior at the same time.[2a] Recently, Li et al. reported that a series of naphthalene derivatives not only act as gelators in various solvents but also behave as LCs.[9] In our previous research,[6a] we have shown that a dendritic gelator of poly(Gly-Asp) can display lyotropic LC behavior in benzyl alcohol at a concentration as low as 6 wt %. For the dendrons studied here, we demonstrate that **1** can show both lyotropic and thermotropic LC behaviors.

It was found that **1** in benzyl alcohol exhibited strong birefringence under polarized optical microscopy (POM) studies when the concentration exceeded 30 wt %. The typical texture of the lyotropic LC of **1** at a concentration of 33 wt % is shown in Figure 3a. Both the thermal POM and DSC experiments indicated that the transition temperature of the isotropic state to lyotropic LC phase is concentration dependent. For example, the transition temperatures of **1** were found to be around 83 and 76 °C for concentrations of 40 and 33 wt %, respectively. The XRD patterns of the lyotropic LC phase of **1** were similar to that observed in the gel state (Figure 4a), wherein the three low-angle peaks with the scattering vector ratio of $1:\sqrt{3}:\sqrt{7}$ can be observed. Moreover, the peaks correspond to the *d* spacing identical to that of the xerogel.

The thermotropic LC texture of pure **1**, which is focal-conic-like, is shown in Figure 3b after the sample was slowly cooled from isotropic phase. Although their textures look different, XRD experiments show that the thermotropic LC phase of **1** possesses characteristics similar to that of lyotropic LC phase and the xerogel as well. In Figure 4b, the sample entered the amorphous state after the temperature reached 150 °C, and higher diffractions became evident at lower temperature. For the two low-angle peaks with the scattering vector ratio of $1:\sqrt{3}$, it can be proposed that **1** self-organized into the columnar hexagonal model too. The *d* spacing is same with that of the corresponding ones found in Figures 2a and 4a. These results suggest that the xerogel and the lyotropic and thermotropic LC phases of **l** in fact share the same molecular packing that forms a hexagonal columnar structure.

Because conventional mesogenic units are not incorporated in **1**, the mesomorphic structures obtained with **1** in solution and bulk state can be ascribed to self-assembly with the whole molecules as building block. However, it is worth noting that **2** can only gel in a few solvents at relatively high concentrations, of which the xerogel shows a lamellar rather than columnar phase. Furthermore, **2** does not exhibit any lyotropic or thermotropic LC properties. The only difference in chemical structure between **1** and **2** is the substituent at the focal point. Therefore, it can be assumed that the bulky and rigid Boc group of **2** may induce significant steric hindrance so that self-assembly is inhibited. As it is only exhibited in the xerogel state, the lamellar structure of **2** is apparently achieved with the assistance of intermolecular interactions between **2** and the solvent such as benzene and toluene at low concentrations. More experiments to elucidate the underlying mechanism are currently carried out in our laboratory.

In summary, we have synthesized two similar dendrons with different focal groups and investigated their mesophase behavior such as gels and liquid crystals. Compound **1** displays gel, lyotropic, and thermotropic LC states with a hexagonal columnar arrangement. In contrast, **2** can only gel a few solvents with a lamellar architecture. Comparison of **1** and **2** demonstrates that a small change of the gelator structure can have huge impact on the self-assembly properties.

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Supporting Information Available: Scheme illustrations, experiment details, TEM images, DSC diagrams, FTIR, and CD spectra (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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