Amino Acid Dendrons

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A Dendron Based on Natural Amino Acids: Synthesis and Behavior as an Organogelator and Lyotropic Liquid Crystal**

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Biomolecules are prone to self-assemble in vivo and in vitro.[1] For example, collagen proteins can self-organize initially into triple helices and then into ordered fibers, gels, and liquid-crystalline (LC) phases through noncovalent forces.[2a,b] Elucidation of the underlying mechanisms is important but tremendously challenging. An alternative is to decipher nature's bewildering tricks with the help of synthetic systems made from natural starting materials.[2] In this context, the natural amino acid based dendrons or dendrimers (NAADs) are of great significance because of their similarity to proteins in composition and topology,[3] as well as their architectural difference from currently prevalent linear model peptides. In addition, potentially chiral and biocompatible NAADs provide exciting possibilities in the creation of new materials for nano- and biotechnology.[4]

However, little attention has been paid to the self-assembly of NAADs,[5] and especially to their gelation and LC properties. Only polylysine dendrimers have been studied as gelators by Smith et al.[6] and gelation is mentioned for dendrimers built from glutamates by Ranganathan et al.[3c,7] Research on NAADs as liquid crystals is even scarcer. Moreover, to the best of our knowledge, there is no report on amino acid based dendrimers that function as gelators and form liquid crystals. We have been interested in the synthesis and self-assembly of dendrimers for many years.[8] Herein, we present the synthesis of a dendron composed of two natural amino acids, glycine and aspartic acid, and its self-assembly which leads not only to organogels but also to lyotropic liquid crystals. Recently, a type of amphiphilic dendritic dipeptide was described by Percec et al.[9] as self-assembling in helical pores. In contrast to their design of an aromatic dendron and a peptide core, our NAADs have peptidic dendrons with a benzyl periphery.

The poly(Gly-Asp) dendrons were convergently synthesized as depicted in Scheme 1. It is well-known that glycine appears at every third position in the predominant sequences of collagen,[2] and aspartic acid is similar to the building unit of a well-investigated linear model peptide, poly(benzyl L-glutamate) (PBLG), which behaves as a gelator and liquid crystal.[10] The dendrons, which resemble the repetitive patterns always found in the sequences of natural fibrous proteins,[2d] were branched iteratively with Gly-Asp dipeptides, instead of with one amino acid as in other NAADs,[11] and without any help from a nonnatural amino acid linkage.

Standard DCC coupling of Boc-glycine and benzyl-protected aspartic acid, which was readily prepared by the benzyl esterification of aspartic acid, gave the branching unit in 60% yield. This is the first generation (**G1**) of the dendron. The second (**G2**) and third generations (**G3**) were synthesized convergently in 35 and 17% yields, respectively, by repeating a two-reaction cycle, that is, by removing the Boc group of the lower-generation dendron with TFA, and then coupling the resultant *N*-deprotected intermediate to the *C*-deprotected **G1** (Boc-**G1**-COOH), prepared by hydrogenative debenzylation of the dipeptide. Currently, one of the major obstacles that hindered the research and applications of NAADs is the tedious process for the purification of the dendritic products.[10] Notably, **G3** is relatively easy to obtain by simple precipitation in water and MeOH consecutively (see Supporting Information). ^{1}H, ^{13}C, two-dimensional, and DEPT NMR techniques, MALDI-TOF mass spectrometry, and elemental analyses were used to verify the structure and purity of the **G3** dendron (see Supporting Information).

We found that **G3** could act as an efficient low-molecular-mass organogelator (LMOG). LMOGs[12c] are a family of low-molecular-mass organic molecules ($M_w \leq 3000$) that can gel organic solvents at very low concentrations through noncovalent forces. LMOGs have attracted considerable renewed interest in recent years, not only because of their interesting roles in materials science and supramolecular chemistry but also because gelation remains poorly understood. Most organogels are achieved through the ordered arrangement of gelators during the cooling of the mixture of LMOGs and organic solvents after heating to form a homogeneous solution.[12] However, a solvent–solvent gel preparation procedure distinguishes **G3** from other LMOGs, including the previously reported dendritic ones.[13] In a typical example, **G3** (0.04 g) was first dissolved in $CHCl_3/CH_3OH$ (9:1 v/v; 6 mL) by sonication. Then, with the addition of ethyl acetate (4 mL), the solution immediately became viscous and gelled within 5 seconds. Meanwhile, a 10-mL gel as dilute as 0.2 wt% (0.98 mM, one **G3** molecule entraps about 9000 solvent molecules) in a 1-cm-diameter test tube could be turned upside down without downward flow of the gel. A thin

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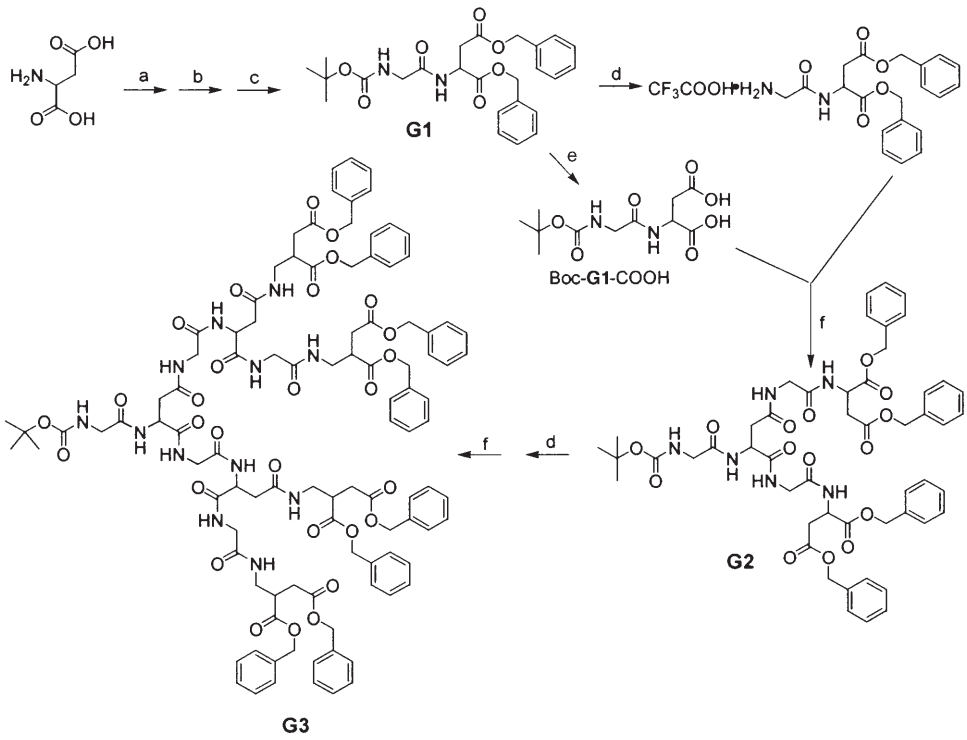
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Convergent synthesis of the first three generations of poly(Gly-Asp) dendrons **G*n*** ($n = 1$–3). Reagents and conditions: a) *p*-toluenesulfonic acid, benzene, benzyl alcohol, reflux; b) CH_3OH, KOH; c) Boc-glycine, DCC, −10 °C; d) TFA, CH_2Cl_2; e) Pd-C, H_2, ethanol; and f) DCC, Boc-**G1**-COOH, *N*-methylmorpholine, NHS, −10 °C. Boc = *tert*-butoxycarbonyl, DCC = dicyclohexylcarbodiimide, TFA = trifluoroacetic acid, NHS = *N*-hydroxysuccinimide.

layer of liquid exuded as time went by, but the main part kept its gel state for more than half a year. The transmission electron microscopy (TEM) image of the **G3** gel showed that the **G3** dendrons self-assembled into a ramified network of intertwined fibers. The width of the fibers ranged from several dozen to more than a hundred nanometers (Figure 1 a). The atomic force microscopy (AFM) image recorded in the tapping mode (Figure 1 c) revealed that the smaller fibers were about 30–70 nm in width, many micrometers in length, but less than 20 nm in height. Considering the convolution effect arising from the finite size of the AFM tips, the real width of the fibers should be even less.

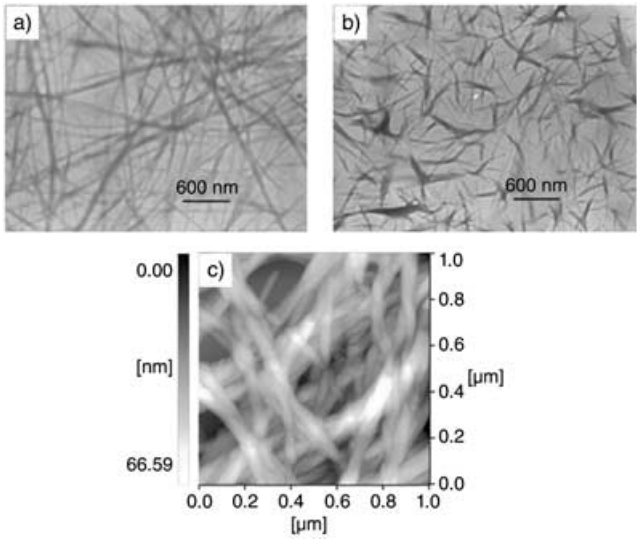


Figure 1. Morphology of **G3**: a) TEM image of a **G3**/CH_3Cl/CH_3OH/ethyl acetate gel; b) TEM image of a **G3**/CH_3Cl/CH_3OH/ethyl acetate suspension; c) AFM image of the **G3**/CH_3Cl/CH_3OH/ethyl acetate gel ([**G3**] = 0.02 wt %).

The gel preparation details have a great effect on gelation. If ethyl acetate was added before **G3** was totally dissolved in $CH_3OH/CHCl_3$, an opaque suspension was formed instead of a gel. TEM shows a rather different morphology of the aggregates in such a suspension (Figure 1 b). In addition to the above case, **G3** dissolved in and gelled a mixture of CH_3OH and THF in several hours. However, the resultant gels were less stable than the CH_3Cl/CH_3OH/ethyl acetate gels at the same concentrations. Neither **G1** nor **G2** formed a gel in the above-mentioned mixed solvents under similar experimental conditions. CH_3OH, $CHCl_3$, CH_2Cl_2, THF, acetone, ethyl acetate, diethyl ether, ethanol, petroleum ether, hexane, cyclohexane, dioxane, acetonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, styrene, water, and benzyl alcohol were tested for the preparation of **G3** gels by the conventional heating and cooling method. Except for benzyl alcohol, none of the single solvents could be gelled by **G3**.

Noncovalent forces, mainly hydrogen-bonding and aromatic-stacking interactions, were proposed to be the driving force for the self-assembly of **G3** dendron. The role of hydrogen bonding in gelation is supported by the fact that the gels changed into clear solutions after the addition of LiCl, which is known to interact strongly with amides and break hydrogen bonds (see Supporting Information). The FT-IR spectrum of the dry gel also revealed characteristic stretching vibrations as a result of hydrogen-bonding interactions in the N–H (3309 cm^{-1}) and C=O (amide I: 1660 cm^{-1}) moieties. However, further proof is needed to verify the presence of hydrogen bonds in the gel state. Other weak interactions may also play an important role in the self-assembly. Fluorescence spectroscopy[14] with pyrene as a probe was employed to examine the effect of benzyl rings. The intensity ratio I_1/I_3 of pyrene emissions is an established index for the polarity of the environment. This ratio decreased as the concentration of **G3** was increased in THF/CH_3OH (9:1; see Supporting Information), which suggests that nonpolar domains were formed as a consequence of the aromatic stacking of peripheral benzyl rings.

What is the relationship between the structure of a native gel and the organization of gelators in the solid state? This is an important question that has puzzled researchers for many years. To address this question in the case of **G3**, as well as to

obtain some hints on its packing pattern in native gels, X-ray diffraction (XRD) was carried out on the native gel, xerogel, and dendrite. No reflection could be detected in the CH_3OH/$CHCl_3$/ethyl acetate gel, presumably as a consequence of strong scattering from the electron-rich $CHCl_3$ solvent. The one-dimensional (1D) XRD pattern of the xerogel is shown in Figure 2. The large scattering halo with a maximum in 2θ at

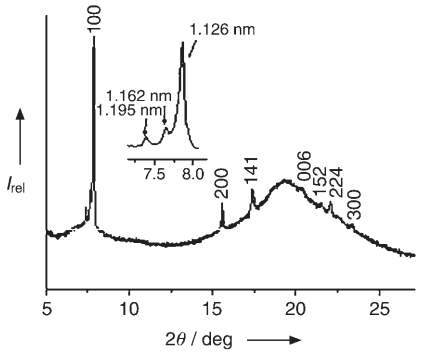


Figure 2. 1D XRD pattern of the **G3**/CH_3OH/$CHCl_3$/ethyl acetate xerogel. The inset shows reflections around $2\theta = 7.86°$.

around 20° (corresponding to a d spacing of ≈ 0.45 nm) indicates that the major portion of **G3** in the xerogel was amorphous. However, the existence of a series of sharp diffractions reveals that the **G3** of the xerogel could partially crystallize. Efforts were made to grow single crystals, but failed. However, **G3** dendrites up to centimeter dimensions were obtained in DMF through evaporation at room temperature for a month. Figure 3 shows a two-dimensional (2D)

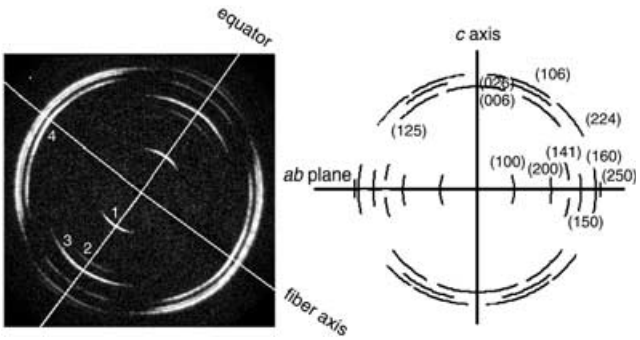


Figure 3. 2D WAXD pattern (left) and its schematic drawing (right) for one fiber-like branch in a **G3** dendrite.

wide-angle XRD (WAXD) pattern obtained from one fiber-like branch of a dendrite, which was collected in the transmission mode with the X-ray incident beam perpendicular to the long axis of the fiber. The sample was rotated through 360° around the long axis during exposure. It was difficult to deduce the precise crystal structure of **G3** because of the scarcity of diffraction lines. However, by assuming that the crystallographic c axis is parallel to the fiber long axis, and that the diffraction lines that correspond to a d spacing of 1.162, 0.581, 0.522, and 0.451 nm are the (100), (200), (141), and (006) planes, respectively (Figure 2), we might tentatively propose an orthorhombic lattice with $a = 1.162$, $b = 2.395$, and $c = 2.706$ nm. As shown in the right-hand side of Figure 3, all the diffraction lines observed can be indexed. The calculated d spacings fitted the measured ones quite well (see Supporting Information). Meanwhile, we noted that the (100) diffraction with a d spacing of 1.162 nm in the dendrite could also be identified in the xerogel (see the inset of Figure 2). Although the intensity is relatively weaker, it indicates that the crystal in the xerogel could have the same structure as the dendrite. However, the coexistence of three peaks with very close d spacings proves that the **G3** crystals are in fact polymorphic. Still assuming an orthorhombic lattice, we found that the strongest diffraction with a d spacing of 1.126 nm and following peaks in the higher 2θ region in Figure 2 could be indexed with $a = 1.126$, $b = 2.331$, and $c = 2.582$ nm, values that deviate only slightly from those proposed for the dendrite. Reexamination of the dendrite testified that polymorphism also occurred. Occasionally, two sets of diffractions could be detected (see Supporting Information) in one fiber. This polymorphism may arise from the rich intra- and intermolecular hydrogen-bonding interactions, which lead to a **G3** molecular packing trapped in different local Gibbs energy minima during crystallization by solvent evaporation.

The gel became a turbid solution and would not regel after it was destroyed by mechanical agitation. Therefore, the morph responsible for gelation is probably not of the most thermodynamically stable phase. Recently, it was proposed[15] that one prerequisite of gel formation is the 1D alignment of gelator molecules. If so, the morph in the gel state should be different from that in the 3D orthorhombic crystals. A structure change, such as crystallization, is quite possible during the formation of a xerogel from a gel by the evaporation of solvents.

G3 can self-organize into lyotropic LC phases in benzyl alcohol. When the concentration of **G3** exceeds a certain limit (about 6 wt%), spherulites and oily streaks (Figure 4a) appeared, as viewed by polarizing optical microscopy (POM). With an increase of the concentration, more spherulites formed and eventually the whole field of view became dominated by a polygonal texture (Figure 4b). The textures can be deformed with pressure and are self-healing. No evidence of microcrystallites was observed. The lyotropic LC

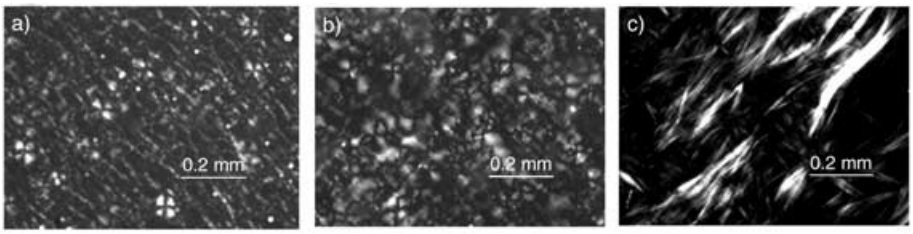


Figure 4. Representative microphotographic textures of **G3** in benzyl alcohol under crossed polarizers. a) Spherulites and oily streaks in 14-wt% samples at room temperature (RT); b) polygonal texture (or focal–conic-like texture) in 30-wt% samples at RT; c) filament texture of 40-wt% samples heated at 10 K min^{-1} and held for 5 min at 100 °C.

behavior of the **G3**/benzyl alcohol phase at several representative concentrations was also examined by differential scanning calorimetry (DSC; see Supporting Information). A single endothermal peak was observed on heating 8-, 14-, and 20-wt% samples. The peak temperature increased monotonously from 60 °C for 8-wt% samples to 80 °C for 20-wt% samples, which was in accordance with the trend of transition of birefringence from anisotropic to isotropic observed by POM.

In the cases of 25-, 30-, 40-, and 50-wt% samples, the DSC heating traces showed a broad endothermic process with two peaks, which indicates two possible transitions. For example, the 40-wt% sample exhibited a lower peak at 88 °C and a higher peak at 95 °C before it completely entered the isotropic state after 105 °C. A new POM texture different to that in Figure 4b developed above the lower transition temperature (Figure 4c). This was also the case for the other samples in the range of 25–50 wt%. The combination of the POM and DSC results suggests that the **G3**/benzyl alcohol mixture may have one lyotropic LC phase below the isotropic temperature at a concentration of 5–20 wt%. As the concentration ranged from 25 to 50 wt%, the samples may have one low- and one high-temperature LC phase prior to the LC-to-isotropic transition.

In contrast to most other LC dendrimers,[16] **G3** is lyotropic and intrinsically mesogenic with relatively flexible chains. It may serve as a good testing bench for the study of the structure–mesophase relationship. The lyotropic LC phase structure of the **G3**/benzyl alcohol mixture at low temperature (below the isotropic temperature for 5- to 20-wt% samples and below the lower transition temperature for 25- to 50-wt% samples) was identified by XRD. In the low 2θ region (Figure 5), a series of scatterings up to the fourth order could be observed for all the concentrations investigated, and the corresponding scattering vector ratios exactly followed 1:2:3:4 which clearly indicated a lamellar structure. This finding agrees well with the spherulites, oily streaks, and polygonal textures observed with POM, which were believed to be the characteristic features of the lyotropic lamellar phase.[17]

Despite varying the concentration, the long period of the lamellae was measured as 4.59 nm. This result indicated that, at low temperature, the samples shared the same lyotropic LC phase where the lamellae coexisted with the solvent. We expected that the lamellae should be a bilayer structure. According to our preliminary computer modeling of the **G3** molecule, the distance from the focal point to the periphery was estimated to be about 2.8 nm if the **G3** molecules were fully extended. Hence, each lamella might consist of two layers of **G3** molecules that are partially interdigitated. In the inner part of the lamellae, the **G3** molecules might associate with their neighbors through hydrogen bonds, while the benzyl rings of the **G3** molecules are packed on the lamellar top and bottom surfaces. More systematic structural and thermodynamic transition property analyses, as well as more morphological studies, are necessary to finally identify the textures and the corresponding phases.

In summary, we have successfully synthesized a novel dipeptide-branched poly(Gly-Asp) dendron (**G3**) capable of self-organizing into organogels and lyotropic LC phases. With a solvent–solvent gel preparation process, the **G3** dendrons self-assembled into a network of intertwined fibers. Both hydrogen-bonding and aromatic-stacking interactions might be responsible for the aggregation. The ordered structure in the xerogel has a close relationship with the orthorhombic packing of **G3** in dendritic crystals. **G3** exhibits lyotropic LC behavior in benzyl alcohol, and a low-temperature lamellar phase with a long period of 4.59 nm can be identified. Fibrous proteins are ubiquitous in nature. Silk fibroin, amyloid, and collagens are but a few remarkable examples.[18] The systems described herein may give us more chance to understand the basic principles governing their supramolecular organization from a new angle different to that offered by linear model peptides. Further investigation is in progress to gain deeper insight into the mechanisms of gelation and mesophase formation, and to unravel the precise molecular-packing patterns of **G3** in the gels, crystals, and liquid crystals. In addition, the applications of such nanostructured materials could be explored as potentially biocompatible systems for drug delivery, molecular recognition, and other diagnostic or therapeutic functions.

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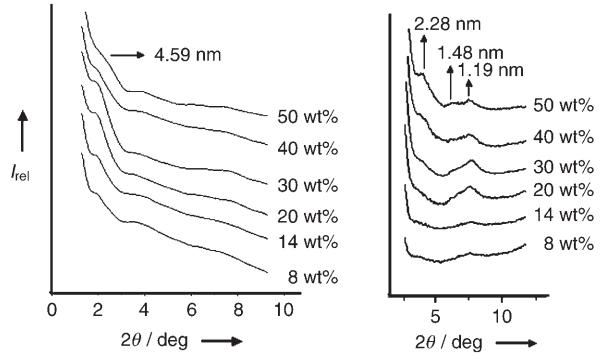

Figure 5. 1D XRD patterns of **G3** in benzyl alcohol. Left: diffraction patterns from $2\theta = 2.5°$ to $2\theta = 12°$ with a prolonged exposure time. Right: overview diffraction patterns at different concentrations.

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