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Peripherally Dimethyl Isophthalate-Functionalized Poly(benzyl ether) Dendrons: A New Kind of Unprecedented Highly Efficient Organogelators

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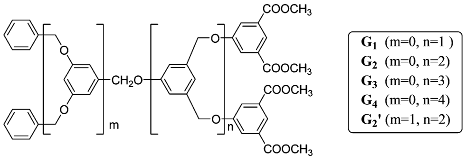
Recently, dendritic gelators have gained much interest due to the advantages of well-defined and tunable structures and the capability of forming multiple noncovalent interactions.[1] So far, a number of physically thermoreversible hydrogel and organogel systems consisting of dendrons or dendrimers with different chemical functionalities have been reported.[2−5] Among the successful examples reported, the incorporation of amide units into the core or the branches of the dendritic organogelators has been considered very necessary for the effective gelation process.[3] In contrast, the design of organogelators, particularly dendritic ones bearing no hydrogen-bonding motifs and/or long alkyl side chains, has been a great challenge.[5] Herein, we report a new kind of unprecedented highly efficient dendritic organogelators, which contain no conventional gelating motifs but form gels in various aromatic and polar organic solvents, and even in aqueous media.

As one essential dendritic structure, poly(aryl ether) dendrons and dendrimers can function as a class of fundamental building blocks, which have been widely used in the construction of nanoscale systems.[3a,b,5−7] Yet their application in underpinning the formation of organogels is rarely reported.[3a,b,5a] In our previous work on the synthesis of functionalized Janus codendrimers,[8] we found that the second-generation poly(benzyl ether) dendron with methyl ester decorations on its periphery could form a strong "jelly" in acetone. This was of particular interest because such a dendron does not bear any conventional gelating motifs such as amides, long alkyl side chains, steroidal groups, and so on.[9] Here we investigated the dendritic structure and generation effect on its gelation properties and attempted to elucidate the mechanistic driving force of this spontaneous self-assembly process.

According to our previous method,[8] a series of peripherally dimethyl isophthalate (DMIP)-functionalized poly(benzyl ether) dendrons were divergently synthesized by using benzylalcohol as starting material and commercially available dimethyl 5-hydroxyisophthalate as the growth unit. The molecular structures of these dendrons are outlined in Scheme 1. Their chemical structures and purities were confirmed by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectroscopy as well as elemental analysis.

The gelation properties of these dendrons were evaluated in various aromatic and polar organic solvents. It was found that the dendron generation exhibited an intriguing effect on the gelation efficiency. $\mathbf{G_2}$ and $\mathbf{G_3}$ displayed a stronger gelation ability than $\mathbf{G_1}$. Both dendrons could form gels in a wide variety of organic solvents including 14 organic solvents and 5 mixed solvents, and the critical gelator concentrations (CGCs) were collected in Table S1 of the Supporting Information (SI). For example, the CGCs of $\mathbf{G_2}$ and $\mathbf{G_3}$ in 2-methoxyethanol were 2.2 and 2.7 mg/mL, indicating that one dendritic molecule could entrap approximately 0.74×10^4 and 1.22×10^4 solvent molecules, respectively. It was particularly interesting to note that $\mathbf{G_4}$ with a globular shape[10] could form gels in toluene, anisole, pyridine, cyclohexanone, benzylalcohol, and a pyridine−water mixture though the CGCs were relatively higher.

Scheme 1. Chemical Structures of Dendritic Organogelators ($\mathbf{G_1}$−$\mathbf{G_4}$ and $\mathbf{G_2'}$)



Furthermore, the dendron bearing a bulky group at the focal point ($\mathbf{G_2'}$) also exhibited efficient gelation in most selected solvents except for cyanobenzene, benzaldehyde, and acetonitrile.

The gel−sol phase transition temperatures (T_{gel}) of the gels in toluene were determined by differential scanning calorimetry (DSC). In general, the stability of the gel network increased with the concentration as exemplified by dendrons $\mathbf{G_2}$ and $\mathbf{G_2'}$ (Figure S3). At 20 mM, T_{gel} for $\mathbf{G_2}$, $\mathbf{G_2'}$, and $\mathbf{G_3}$ decrease in the order 76.0, 49.4, and 45.4 °C, suggesting that $\mathbf{G_2}$ has the best thermal stability of gel.

The aggregation structures of the dendritic xerogels were investigated by scanning electron microscopy (SEM). Fiberlike or ribbonlike morphologies for different generation dendrons and/or in different organic solvents were observed (Figure 1 and Figure S4). For example, the xerogels of $\mathbf{G_2}$ and $\mathbf{G_3}$ from benzene exhibited an entangled network of thin solid fibers. Some fibers were found to be bundled with diameters of 50−150 and 30−300 nm, respectively. Notably, the morphologies of $\mathbf{G_1}$ and $\mathbf{G_4}$ are different (Figure S5−S9). $\mathbf{G_1}$ was distributed into a homogeneous aggregation of straight fibers with 200−600 nm diameters. In contrast, $\mathbf{G_4}$ showed a porous globular morphology ($\sim$2 μm particles) with a dense network of fibrillar structure inside. The morphological properties were further confirmed by transmission electron microscopy (Figure S10) and atomic force microscopy (Figure S11).

The crystal structure and packing diagram of $\mathbf{G_1}$ were shown in Figure 2. It was noted that one of the peripheral DMIP rings (electron-deficient "head") was coplanar with the internal benzyl ring (electron-rich "tail"). The two neighboring extended planes were stacked in head-to-tail pairs with interplanar distances of ca. 3.42 Å (Figure 2B), indicative of strong $\pi-\pi$ interactions. Intermolecular weak CH−π interactions (2.59 Å) and nontypical hydrogen bonding (2.42−2.58 Å) were also found in the crystal structure (Figure S13). To the best of our knowledge, this is the first example of intermolecular assembly of DMIP-based systems that form supramolecular dendritic aggregates.

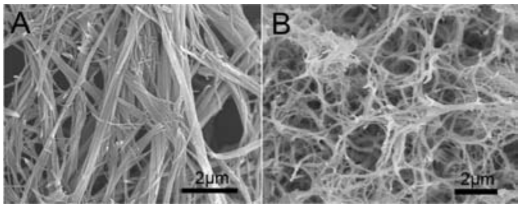


Figure 1. SEM images of the dendritic xerogels of $\mathbf{G_2}$ (A) and $\mathbf{G_3}$ (B) (scale bar = 2.0 μm).

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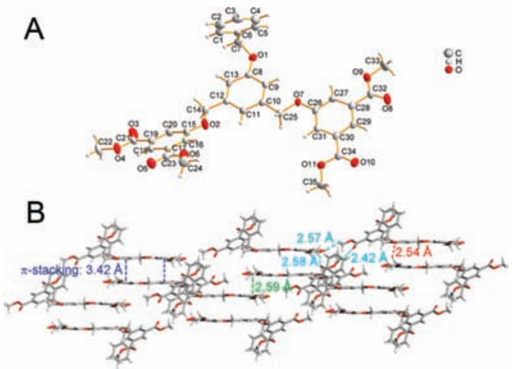

Figure 2. (A) Molecular structure of G_1 in the crystal. (B) $\pi-\pi$ stacking, $CH-\pi$, and nontypical hydrogen bonding in the crystal of G_1.

The formation of $\pi-\pi$ stackings of these dendrons in solution and the gel state was also confirmed by concentration-dependent (CD) and temperature-dependent (TD) ^1H NMR studies.[9d,11] In the CD-^1H NMR experiments performed in 1.1−36.6 mg/mL solutions of $\mathbf{G_1}$ in $CDCl_3-CCl_4$, the increase in the concentration resulted in the slight upfield shifts of the resonance signals for the aromatic protons on the peripheral DMIP rings and the internal benzyl rings (Figure S14). Regarding the TD-^1H NMR experiments, these resonance signals were found to be gradually shifted downfield when the temperature increased from 10 to 50 °C (Figure S15). Notably, the signals corresponding to the benzyl ring at the focal point remained constant. The ^1H NMR spectra of $\mathbf{G_2}$ (8.0 mg/mL) in CD_3CN were also recorded at different temperatures. A similar signal-shift trend was observed upon warming from 20 to 90 °C (Figure S16). In addition to the shifts, these signals experienced a dramatic broadening below 60 °C, which is consistent with the virtually complete gel formation under these conditions.

In addition, the $\pi-\pi$ interactions were further evidenced by solvent titration experiments and a powder X-ray diffraction (PXRD) study. The fluorescence intensity of $\mathbf{G_2}$ drastically decreased when the volume ratio of tetrachloromethane to chloroform was increased in the binary solvent (Figure S17). This result indicated the enhancement of $\pi-\pi$ interactions, which is consistent with the signal-shift trend in the ^1H NMR spectra (Figure S18). Furthermore, a prominent reflection characteristic of a typical $\pi-\pi$ stacking distance was observed in the wide-angle region at 3.5 Å of the PXRD patterns (Figure S19).[12,9d]

To evaluate the role of the peripheral methyl esters in the self-assembly process, we synthesized several analogous $\mathbf{G_2}$ dendrons that differed only in the peripheral ester groups (for molecular structures, see Scheme S1). The CGCs of these dendrons in various solvents were collected in Table S1. As expected, dendron $\mathbf{G_2}$**-Ph** without any ester groups is very soluble in most of the selected solvents, and gelation was not observed. Introducing one methyl ester on the peripheral phenyl ring (**3-**$\mathbf{G_2}$) enhanced self-assembly of these dendritic molecules. However, stable gels could only form under high CGCs in 9 solvents. When methyl ester groups were replaced by ethyl esters ($\mathbf{G_2}$**-Et**), an increase in solubility was observed. Stable gels were formed in only 5 solvents and with high CGCs. Surprisingly, in the case of dendron **3,4-**$\mathbf{G_2}$ which bears methyl esters in the 3,4-position, no gelation was observed in all selected solvents. In addition, if ester groups in $\mathbf{G_2}$ were replaced by trifluoromethyl groups ($\mathbf{G_2\text{-}CF_3}$), gelation was not observed in most selected solvents except for benzylalcohol. All these results suggested that the peripheral DMIP motifs played an important role in the self-assembly of these dendritic molecules.

Furthermore, the linear oligo(benzyl ether) $\mathbf{LG_2'}$ bearing DMIPs as pendant groups, which is identical in chemical composition to $\mathbf{G_2'}$ (for details, see SI), was also synthesized. It was found that $\mathbf{LG_2'}$ was an inefficient gelator (Table S1), suggesting that the dendritic architecture is also critical in forming the self-assembled gel.[4]

In conclusion, we have established the first example of large monodisperse peripherally DMIP-functionalized poly(benzyl ether) dendritic organogelators without amides or long alkyl chains. Their gelation property is highly dependent on the nature of the peripheral groups, the dendritic architecture, and generation. The multiple strong $\pi-\pi$ stacking interactions due to the peripheral DMIP motifs are the key contributor in forming the self-assembled gel. Further study on detailed structure−property relationships of these dendrons and their applications in functional nanomaterials is in progress.

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Supporting Information Available: Synthetic and experimental details, and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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