Gelators

A Systematic Study of Peripherally Multiple Aromatic Ester-Functionalized Poly(benzyl ether) Dendrons for the Fabrication of Organogels: Structure–Property Relationships and Thixotropic Property

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Abstract: A new class of peripherally multiple aromatic ester-functionalized poly(benzyl ether) dendrons and/or dendrimers with different focal point substituents, surface groups, interior structures, as well as different generations have been synthesized and their structure-property relationships with respect to their gelation ability have been investigated systematically. Most of these dendrons are able to gel organic solvents over a wide polarity range. Evident dendritic effects were observed not only in gelation capability but also in thermotropic, morphological, and rheological characterizations. It was disclosed that subtle changes in peripheral ester functionalities and interior dendritic structures affected the gelation behavior of the dendrons significantly. Among all the dendrons studied, the second- and third-generation dendrons G_0G_2 -Me and G_0G_3 -Me with dimethyl isophthalates (DMIP) as peripheral groups exhibited the best capability in gelation, and stable gels were formed in more than 22 aro-

Introduction

As one of the most efficient approaches for the construction of highly ordered nanoscale functional self-assemblies, the discovery and application of new gelators has gained extraordinary attention.^[1] Dendritic gelators, the newest member in gel family, exhibit unique properties different from those of the small molecule gel and traditional polymer gel systems due to their well-defined three-dimensional macromolecular architec-

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	Supporting information for this article is available on the WWW under
30000C	http://dx.doi.org/10.1002/chem.201400157.

matic and polar organic solvents. The lowest critical gelation concentration (CGC) reached 2.0 mg mL⁻¹, indicating that approximately 1.35×10^4 solvent molecules could be entrapped by one dendritic molecule. Further study on driving forces in gel formation was carried out by using a combination of single-crystal/powder X-ray diffraction (XRD) analysis and concentration-dependent (CD)/temperature-dependent (TD) ¹H NMR spectroscopy. The results obtained from these experiments revealed that the multiple π - π stacking of extended π -systems due to the peripheral DMIP rings, cooperatively assisted by non-conventional hydrogen-bonding, is the key contributor in the formation of the highly ordered supramolecular and fibrillar network. In addition, these dendritic organogels exhibited unexpected thixotropic-responsive properties, which make them promising candidates with potential applications in the field of intelligent soft materials.

ture and diversity in functionalization, and thus have become a new type of promising candidate in the research of gel phase materials.^[2-16] The dendritic architectures render them capable of being incorporated with different functional groups into the core, the inner and/or outer layers, providing multirecognition sites for self-assembly. However, due to their more complex molecular structures (compared with the low-molecular-weight gelators), it is still difficult to manipulate and balance various weak interactions, including hydrogen bonding, electrostatic interactions, solvophobic forces, π - π interactions, and van der Waals forces, to meet the requirements for gel formation. In addition, the highly structural tunability of dendritic molecules provides an ideal platform for the systematic study of the structure-property relationships of dendritic gel systems. However, an in-depth understanding of the gelation mechanism, which will guide the rational design of new dendritic gelators, is less reported. Therefore, the discovery of new types of dendritic organogelators has been a great challenge.

Among the successful dendritic organogelators reported to date, a typical hydrogen-bonding-dominated self-assembling protocol has been mainly utilized in the molecular design by selecting an amide unit as the main gelation motif.^[5-11] In



2000, Aida and co-workers reported the first example of dendritic organogel by introducing a dipeptide into the focal point of ester-terminated Fréchet-type dendrons.^[5] It was demonstrated that the gelation was mainly induced by hydrogenbonding interactions. The role of the ester-terminated Fréchettype dendron in the self-assembly processes was described as supplementary van der Waals forces. From 2001, Smith and coworkers have systematically studied both one-component and two-component dendritic organogels based on poly(lysine) dendrimers with amide dendritic branches, and disclosed that the intermolecular hydrogen bonding played an important role in the gel-phase assembly.^[7] However, these efficient dendritic gelators were limited to low generations because negative steric factors might become increasingly dominant for high-generation dendrimers, hindering the anisotropic self-assembly.^[7c] Distinguished from these core- and skeleton-amide functionalized dendritic gelators,^[5-11] self-assembly dominated by the peripheral functional groups of dendritic molecules allows straight and cooperative multivalent interactions between intermolecular multiple gelation motifs, which has proven to be beneficial for highly efficient hydrogel formation.^[3,4] More importantly, the capability to accommodate a functional group at the core or the focal point renders the peripherally functionalized dendritic gelators more attractive for applications in the fabrication of functional nanomaterials. Surprisingly, in sharp contrast to dendritic hydrogels, dendritic organogelators with gelation motifs at the periphery are rarely reported.^[14, 17]

In our previous communication on the serendipitous discovery of a new kind of dendritic organogelator,^[17] peripherally dimethyl isophthalates (DMIP)-functionalized poly(benzyl ether) dendrons without any conventional gelation motifs, such as amides, long alkyl side chains, and steroidal groups, showed unprecedented high efficiency in gelating aromatic and polar organic solvents, and even aqueous media. Different from the gel-phase self-assembly of the core- and skeleton-amide functionalized dendritic gelators, which is dominated by typical hydrogen-bonding,^[5-11] such peripherally functionalized poly(benzyl ether) dendrons represent a new type of dendritic gelators whose assembly is dominated by cooperative multi-types of non-covalent-bonding interactions resulting from peripheral groups. To give an in-depth insight of this new dendritic gel system, herein, we report the design and synthesis of series of peripherally aromatic ester-functionalized poly(benzyl ether) dendrons by altering the component and/or structure of the peripheral aromatic ester groups, dendritic branches, and the focal point moiety. A systematic study on structure-property relationships was pursued to obtain fundamental structural parameters for molecular design, which focused on the mechanism elucidation of the self-assembly processes. Furthermore, the unexpected thixotropic-responsive properties of these dendritic organogels were also investigated.

Results and Discussion

Molecular design and synthesis

To elucidate the effect of peripheral ester groups, poly(benzyl ether) skeleton, and focal-point functionalities on gelation properties, four categories of peripherally aromatic ester-functionalized poly(benzyl ether) dendrons were designed as illustrated in Scheme 1, based on the molecular structure of the best dendritic organogelator G_0G_2 -Me demonstrated in our preliminary research. To evaluate the effect of different peripheral ester substituents on gelation properties, methyl, ethyl, or benzyl ester groups were introduced into the outer phenyl rings of G_0G_2 dendron, in a 3-mono-, 4-mono-, 3,4-di-, or 3,5disubstituted manner (category 1). Fréchet dendrons of generation 1 to 3 were attached to the focal point of G_0G_2 -Me to see how bigger dendritic wedges affect the gelation properties (category 2). Dendrons in the same molecular formula of G_0G_2 -Me with variations in backbone structure, such as the "reversed" Fréchet-type dendron G₀G₂'-Me bearing peripheral DMIP motifs and 3,4-branching analogues of G₀G₂-Me (3,4-G₀G₂-Me-N1 and 3,4-G₀G₂-Me-N2) compose the third category. The fourth category includes the dendrons with similar architecture as G_0G_2 -Me, but of different generation from 1 to 4.

According to our previously reported method,[17,18] sixteen peripherally aromatic ester-functionalized poly(benzyl ether) dendrons/dendrimers, as described above, were divergently synthesized by using benzyl alcohol or Fréchet dendritic benzyl alcohols as a starting material and commercially available dimethyl 5-hydroxylisophthalate and/or dimethyl 4-hydroxylphthalate as the generation growing agent, through a repetitive Mitsunobu coupling and ester reduction sequence. Dendrons with different aromatic ester functionalities other than DMIP were also synthesized by using diethyl 5-hydroxylisophthalate, dibenzyl 5-hydroxylisophthalate, dimethyl 4-hydroxylphthalate, methyl 3-hydroxybenzoate, or methyl 4-hydroxybenzoate as the reactant in the final Mitsunobu reaction. In addition, poly(benzyl ether) dendron G₀G₂-Ph without surface ester groups and a linear oligo(benzyl ether) G1-8-COOMe bearing 4 DMIP groups as pendants were also prepared for comparison. Chemical structures and purities of all the compounds synthesized were confirmed by using ¹H/¹³C NMR spectroscopy and MALDI-TOF mass spectrometry as well as elemental analysis (see the Supporting Information for details).

Gelation abilities of dendritic organogelators

In general, gelation properties change dramatically along with the small structural variation in the gelator molecule depending on the solvent used. For better understanding of the structure–property relationships, the gelation abilities of the synthesized dendritic macromolecules were investigated in various organic solvents and mixed solvents by a "stable to inversion" method; the results are summarized in Table 1, and some key features are discussed.

Chem. Eur. J. 2014, 20, 7069 – 7082





Scheme 1. Schematic structures of poly(benzyl ether) dendritic macromolecules and oligomer.

Impact of peripheral ester functionalities

As one important methodology for structural alteration, modification of the dendritic periphery with different functionalities will obviously affect the properties of dendrons/dendrimers, such as chemical reactivity, glass transition temperature, and especially, the solubility. Considering the nature of the complicated phase-separation system of the gel, it is of special interest to fine-tune the gelator solubility upon balancing the amphiphilic molecular structure. It has been demonstrated in the dendritic organogel systems that the gelator solubility has a subtle influence on gelation properties, such as T_{gel} and critical gelation concentration (CGC), as well as the cooperative self-assembling level.^[19] Therefore, in this work, we firstly investigated the role of the peripheral ester functionalities of the poly(benzyl ether) dendrons on gelation properties, including ester species, substituent number, and substitution position of the ester groups.

As shown in Table 1 and Table S1 (the Supporting Information), the critical gelation concentrations of dendrons G_0G_2 in category 1 in various organic and mixed solvents were collected. Dendron G_0G_2 -Ph without ester groups at the periphery was soluble in most solvents tested, and no gelation phenomenon was observed. In sharp contrast to dendron G_0G_2 -Ph, the DMIP-functionalized dendron G_0G_2 -Me is the most efficient gelator among the dendrons screened, which could gel 15 aromatic and polar organic solvents and 7 mixed solvents (includ-



	G₀G₁-Me	G ₀ G ₂ -Me	3,4-G ₀ G ₂ -Me-N1	3,4-G ₀ G ₂ -Me-N2	G₀G₂′-Me	G₀G₃-Me	G₀G₄-Me	G ₁ G ₂ -Me	G ₂ G ₂ -Me	G₃G₂-Me
Solvents										
Toluene	G (30.3)	G (3.3)	PG	PG	G (20.0)	G (5.2)	G (33.8)	G (5.0)	G (16.2)	PG
Benzene	G (52.6)	G (2.2)	G (22.2)	G (22.8)	G (20.8)	G (10.1)	G (52.7)	G (4.5)	G (52.0)	S
Anisole	PG	G (8.2)	S	S	G (18.0)	G (2.6)	G (33.8)	G (33.5)	S	S
Phenyl ether	PG	G (3.7)	PG	PG	G (11.5)	G (2.8)	PG	G (16.7)	S	S
Pyridine	S	G (11.5)	PG	S	G (16.8)	G (6.9)	G (39.0)	G (28.0)	S	S
Cyanobenzene	PG	G (14.5)	S	S	G (29.6)	G (13.0)	S	S	S	S
Benzaldehyde	S	G (32.7)	S	S	PG	G (18.0)	PG	PG	S	S
Ethyl acetate	PG	G (18.0)	G (14.0)	S	G (16.0)	G (6.9)	PG	G (32.8)	PG	PG
Cyclohexanone	PG	G (10.7)	PG	PG	G (23.3)	G (3.4)	G (50.8)	G (16.5)	PG	S
Acetone	S	G (3.9)	G (6.2)	G (35.6)	G (12.5)	G (3.2)	Р	G (11.6)	G (12.0)	G (8.5)
Acetonitrile	Р	G (6.6)	G (12.3)	G (16.8)	G (11.3)	G (4.4)	Р	Р	G (27.5)	I
2-Methoxyethanol	S	G (2.2)	G (8.1)	G (33.3)	G (19.1)	G (2.7)	Р	G (6.6)	G (12.9)	G (6.3)
Benzyl alcohol	G (47.3)	G (4.3)	G (9.6)	G (18.9)	G (8.4)	G (8.0)	G (33.0)	G (3.6)	G (20.0)	G (10.7)
Tetrachloromethane	G (43.6)	G (2.4)	G (13.7)	G (13.0)	G (3.6)	G (2.0)	G (21.0)	G (3.1)	G (3.1)	G (31.5)
1,2-Dichloroethane	S	G (10.0)	PG	PG	PG	G (12.2)	G (36.0)	PG	S	S
$CHCI_3/CH_3CN = 1:9$	PG	G (3.2)	G (8.4)	G (21.8)	G (19.7)	G (2.9)	Р	G (12.0)	G (21.0)	G (10.0)
$CHCl_3/CCl_4 = 1:9$	PG	G (2.7)	G (16.6)	G (7.1)	G (22.3)	G (2.5)	Р	G (3.7)	G (36.8)	PG
$THF/CH_{3}OH = 3:1$	Р	G (7.3)	PG	PG	G (15.5)	G (6.0)	PG	G (16.8)	PG	PG
$THF/H_2O = 3:1$	Р	G (4.4)	PG	Р	G (8.1)	G (5.1)	PG	G (12.4)	S	PG
Pyridine/H ₂ O = 4:1	Р	G (2.0)	G (6.0)	G (7.3)	G (10.9)	G (5.1)	G (33.0)	G (1.8)	G (28.5)	G (15.8)
Anisole/CCl ₄ =3:2	Р	G (5.1)	PG	G (32.5)	G (42.0)	G (5.5)	PG	G (21.0)	S	S
Anisole/Hexane = 1:1	G (36.0)	G (2.8)	G (26.6)	PG	G (10.6)	G (2.1)	Р	G (38.2)	G (13.7)	Р

Table 1. Galation properties and critical galator concentrations (CGCs) of dendrons and dendrimers in various organic solvents and mixed solvents at

ing water-containing mixtures) with the lowest CGC of 2.0 mg mL⁻¹. When methyl ester groups were replaced by ethyl esters (G₀G₂-Et) or benzyl esters (G₀G₂-CH₂Ph), decreased gelation abilities were noticed. Stable gels were only formed in five solvents and mixed solvents with high CGC values. Surprisingly, gelation was not detected for the peripherally dissymmetric dendron 3,4-G₀G₂-Me in all the selected solvents. Reducing the substituent number of methyl ester to one per phenyl ring also caused a decrease in the gelation efficiency. The positive effect of molecular symmetry was also found for dendron 4-G₀G₂-Me, exhibiting a better performance than 3- G_0G_2 -Me, which was more soluble in most organic solvents. All these results suggest, as we expected, that the gelation ability of the poly(benzyl ether) dendrons could be finely tuned by peripheral modification, and DMIP is demonstrated to be the most efficient motif for gelation.

Impact of focal point attachment of Fréchet dendrons

Peripheral DMIP-functionalized co-dendrimers bearing a Fréchet dendron at the focal point, $\mathbf{G}_m\mathbf{G}_2$ -**Me** (m=1-3), were then tested in selected solvents and compared to the focal benzyl ether-substituted analogue $\mathbf{G}_0\mathbf{G}_2$ -**Me**. An obvious trend of gelation ability variation was found. When increasing the generation of the focal Fréchet dendron from 1 to 3, the gelator solubility increased gradually in aromatic solvents accompanied with the decrease in gelation efficiency. As shown in Table 1, $\mathbf{G}_1\mathbf{G}_2$ -**Me** formed gels in 18 tested solvents, whereas $\mathbf{G}_2\mathbf{G}_2$ -**Me** only gave gels in 11 solvents. More importantly, the co-dendrimer $\mathbf{G}_3\mathbf{G}_2$ -**Me** bearing a bulky dendritic wedge at the focal point also exhibited efficient gelation in 6 solvent systems, including hydrogen-donating solvents, such as acetone, 2-methoxyethanol, and benzyl alcohol. The lowest CGC of G_3G_2 -Me reached 6.3 mg mL⁻¹ in 2-methoxymethanol. Considering the high molecular weight of the co-dendrimer, this CGC value is comparable to those of the best low-molecular-weight gelators. The highly structural tolerance of focal point attachment from the viewpoint of gelation ability indicates that these dendritic gelators with peripheral functionalities could be used as an efficient gelation motif for the development of new functional nanomaterials by easy post-functionalization at the focal point.^[20]

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Impact of the backbone structure

To elucidate the effect of the structure of dendritic backbone on gelation ability, dendrons identical in chemical composition of G_0G_2 -Me were synthesized for comparison, including G_0G_2 '-Me, a Fréchet-type dendron possessing peripheral DMIP motifs with a "reversed" dendritic backbone, and 3,4-branching analogues of G_0G_2 -Me (3,4- G_0G_2 -Me-N1 and 3,4- G_0G_2 -Me-N2) at different branching points of generation growth. A linear oligo(benzyl ether) G_1 -8-COOMe with DMIP motifs as pendant groups was also prepared. As shown in Table 1 and Table S1 (the Supporting Information), the monodispersed dendron G_0G_2 '-Me exhibited comparable gelation behavior as G_0G_2 -Me from the view-point of solvent scope, but the CGC values were a little bit higher. The symmetry of the dendritic architecture was noticed to influence the gelation ability of the gelators. Increases of CGC values in most aromatic solvents were observed for both **3,4-G**₀**G**₂-**Me**-**N1** and **3,4-G**₀**G**₂-**Me**-**N2**. In sharp contrast to dendron **G**₁**G**₂-**Me**, a stable gel of linear analogue **G**₁-**8-COOMe** could only exist in THF-CH₃OH (3:1, v/v) mixture, suggesting that the dendritic architecture is critical in forming the self-assembled gels.

Impact of the dendritic generation

The impact of dendron generation on gelation ability is much more difficult to quantify than it is to describe due to the considerable changes of multi-parameters related to the generation growth, including the size of dendron, the configuration of molecule, and more importantly for peripherally functionalized poly(benzyl ether) dendrons, the amount of peripheral functionalities. In our study, dendron generation exhibited an intriguing effect on gelation ability (Table 1 and Table S1, the Supporting Information). Similar to the reported results of other dendritic gelators, moderate generation (generally 2 to 3) of the dendron is superior to low generation for gel formation, dendrons $G_0G_2\mbox{-}Me$ and $G_0G_3\mbox{-}Me$ displayed much better gelation ability than G_0G_1 -Me. Both dendrons formed stable gels in all organic solvents investigated, and proved to be the most efficient gelators with CGC values mostly less than 1 wt.%. It is of particular interest to witness that dendron ${\bf G}_0 {\bf G}_4 \text{-} {\bf Me}$ with a globular shape $^{[21]}$ also exhibited better gelation behavior than G_0G_1 -Me, gels were formed in 7 solvents, though the CGC values were relatively higher. This is guite different from the performance of amides or peptide-containing dendritic gelators, whose self-assembly is dominated by typical hydrogen bonding.

Thermotropic behavior of dendritic gels

The structure–property relationships were also investigated in the thermotropic behavior of dendritic xerogels and native gels with focuses on the generation influence based on two series of dendrons, G_0G_n -Me and G_mG_2 -Me, showing apparent "dendritic effects". A positive "dendritic effect" of dendrons G_0G_n -Me has been demonstrated along with the generation increasing for both xerogels and wet gels, whereas, a negative "dendritic effect" of the focal point-functionalized co-dendrimers G_mG_2 -Me has been identified.

The glass transition temperatures (T_g) of xerogels^[5] prepared by a freeze-drying method in benzene were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min⁻¹ from 0 to 140 °C (Figure S1, the Supporting Information). For dendrons G_0G_n -Me, upon increasing the dendron generation from 1 to 4, a steady enhancement of T_g was inspected from 36.4 °C for G_0G_1 -Me to 55.4, 71.8, and 73.1 °C for G_0G_2 -Me, G_0G_3 -Me, and G_0G_4 -Me, respectively. On the contrary, the T_g for co-dendrimers G_mG_2 -Me gradually decreased upon generation elevation of the focal point-attached Fréchet dendron; 55.4, 49.5, and 47.2 °C for G_0G_2 -Me, G_1G_2 -Me, and G_2G_2 -Me were recorded, respectively.

The effect of concentration on gel–sol phase-transition temperature (T_{gel}) of wet gels in toluene was further examined by using the tube-inversion method. For all gelators tested, a regu-



Figure 1. Effect of concentration on T_{gel} of G_0G_2 -Me, G_0G_3 -Me, G_1G_2 -Me, G_2G_2 -Me, and G_0G_2' -Me as measured by inverse flow method (solvent: toluene).

lar increase in T_{gel} was observed as the concentration of gelator molecule was elevated, suggesting an increase in the thermostability of the gel. The generation effects were found to be similar to those of xerogels. As shown in Figure 1, the secondgeneration dendron G_0G_2 -Me had a T_{gel} value of 66°C at the concentration of 10 mm, the value increased to 71 $^{\circ}$ C for **G**₀**G**₃-Me and 73 °C for G_0G_4 -Me. The first-generation dendron G_0G_1 -Me was a solution at this concentration. As the generation of the focal Fréchet dendron increased from 0 to 2, the T_{ael} of codendrimers G_mG₂-Me decreased dramatically with the gel samples at the same concentration. For example, the T_{gel} for G_0G_2 -Me was 75.0 °C at 20 mm, whereas the T_{gel} of G_1G_2 -Me dropped to 49.0 °C, and the lowest T_{gel} of 34 °C was observed for G₂G₂-Me. The co-dendrimer G₃G₂-Me bearing the biggest poly-(benzyl ether) dendron as the focal point attachment was a solution at this concentration. The wet gel of dendron G_0G_2 '-Me with a reversed backbone structure showed lower thermostability compared with that of **G**₀**G**₂-**Me**.

Morphological properties of dendritic gels

The morphological properties of xerogels of these dendrons/ dendrimers were studied in detail by scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM), and transmission electron microscopy (TEM; Figure 2 and Figures S2-S5, the Supporting Information). Although fibrillar assemblies were found to be essential for most gel samples, the generation effect on the gel morphology was still distinctive. For example, in the xerogels of dendron series of $\mathbf{G}_{0}\mathbf{G}_{n}$ -Me (n = 1, 2, 3, 4) from benzene, the generation growth caused a notable variation in morphology. Dendron G_0G_1 -Me was distributed into aggregates of straight ribbons with large diameters of 200-600 nm. Long fibers with a homogeneous diameter of 50–150 nm were observed for dendron G₀G₂-Me, and bundles of entangled fibers composed a crossed network. Fibers as the exclusive aggregates were also confirmed in G₀G₃-Me samples, but the fiber diameter and shape were dif-





(Figure 3). First, to assess the dy-

namic nature and relaxation modes of these dendritic gels, the oscillatory frequency sweep measurements were carried out at the same concentration (Fig-

ure 3 A and 3 B). The frequency

sweep curves of these dendritic gels were consistent with the behaviors as true gels: both the storage modulus (G') and the loss modulus (G'') exhibited

a slight frequency dependence in the frequency range of 0.1-

100 rad s⁻¹ with G' an order of

magnitude larger than G", implying that the gels are typical elas-



Figure 2. SEM and ESEM images of freeze-dried dendritic xerogels from benzene: A) and E) G_0G_1 -Me; B) and F) G_0G_2 -Me; C) and G) G_0G_3 -Me; D) and H) G_0G_4 -Me. Scale bar is 2.0 and 5.0 μ m, respectively.

ferent from those of G_0G_2 -Me. In addition to the curled fiber bundles of 80–200 nm that intertwined to construct the network skeleton, imperceptibly thin fibers of 30–80 nm in diameter filled in to connect the network, which was only observed in ESEM images possibly due to the mild conditions for sample preparation. In contrast, the essential morphology of G_0G_4 -Me aggregates were three-dimensional globular particles of diameter 2–3 µm, which were porous with a dense network of branched fibrillar structures inside. Imperceptibly thin fibers were also found on the surface of these particles to facilitate the conjugation of particles. This distinct morphology behavior is probably ascribed to the special dendritic molecular shape and large amount of the peripheral functionalities (16 DMIP groups with 32 methyl esters per dendron). The morphology changes were also confirmed by TEM images (Figure S2, the

Supporting Information). In addition, no evident differences in morphology behaviors of dendrimers G_mG_2 -Me (m=0, 1, 2) were discovered (Figures S3 and S4, the Supporting Information). The morphologies of the xerogels with respective solvents were also investigated by using SEM. For example, a very dense fiber-like morphology for G_0G_3 -Me in different organic solvents was observed (Figure S5, the Supporting Information).

Rheological behavior of dendritic gels

To receive additional information of the structure–property relationships, rheological experiments with dendritic gels of G_0G_n -Me (n=2, 3), G_mG_2 -Me (m=1, 2), and G_0G_2' -Me formed in toluene were conducted dynamic moduli (G' and G'') versus time at 20 °C are shown in Figure 3C and 3D. For all the dendritic gelators tested, the modulus values kept constant within a long period of time, indicating the stability of the gel network was maintained once it was formed. More importantly, dendritic generation effects were also observed for both series of dendrons, G_0G_n -Me and G_mG_2 -Me. The organogel rigidity determined by G' followed the increasing trend as: G_0G_2' -Me $< G_2G_2$ -Me $< G_1G_2$ -Me < G_0G_2 -Me $< G_0G_3$ -Me. The trends for G_0G_n -Me and G_mG_2 -Me are in agreement with those acquired from the study of thermotropic behavior as mentioned above. The dendritic gel of G_0G_3 -Me displayed better rigidity associated with an elastic gel structure than that of G_0G_2 -Me. For example, the storage modulus G' for G_0G_3 -Me at 10 mM is 32 kPa, which is higher than

tic rather than viscous soft matter. In addition, the variation of



Figure 3. Storage modulus G' and loss modulus G' for dendritic organogels formed in toluene (10 mm) at 20 °C as a function of A) and B) oscillation frequency with a strain of 0.03 %, C) and D) time with a frequency of 1 Hz and a strain of 0.03 %.



19 kPa for G_0G_2 -Me, suggesting a multivalent effect. As the generation of the focal Fréchet dendron increased from 0 to 2, the storage modulus G' of G_mG_2 -Me decreased at the same concentration. For example, the G' for G_0G_2 -Me was 19 kPa at 10 mM, whereas G' of G_1G_2 -Me dropped to 16 kPa, and the lowest G' of 10.8 kPa was observed for G_2G_2 -Me. Surprisingly, the gel G_0G_2' -Me showed the weakest rigidity among the gelators tested, which is different from the results of the thermostropic experiments, in which G_0G_2' -Me showed better thermostability than the focal point-functionalized co-dendrimers G_1G_2 -Me.

Detailed measurements of rheological properties for determining the influence of gelator concentration on storage and loss moduli were also carried out. Figures S6 and S7 (the Supporting Information) show the time and frequency sweep curves of dendritic gels of G₀G₂-Me and G₀G₃-Me formed in toluene at different concentrations. For both organogels, the storage modulus G' and the loss modulus G" increased as expected with the increasing of dendritic gelator concentration from 2 to 12 mm, which is in accordance with the rheological property of a true gel. The mechanical properties of the resulting gels from G₀G₃-Me are substantially superior to those of G_0G_2 -Me. These differences should be ascribed to the different mode and level of self-assembly relating directly to the variation of the dendritic structure.^[22] From the SEM images of xerogels from toluene (see Figure S8, the Supporting Information), well-intertwined thicker fibers in a curved shape were found for dendron $G_0G_3\mathchar`-Me$, whereas $G_0G_2\mathchar`-Me$ showed a straight and looser network structure.

Driving forces in gel formation

To gain better insight into the possible relationships between dendritic structure parameters and molecular recognition, the key issue is to reveal the driving forces responsible for the spontaneous supramolecular process of self-assembly. X-ray diffraction experiments and elaborate ¹H NMR studies were applied to this investigation.

X-ray diffraction experiments of low generation dendrons

In our previous work,^[17] it has been demonstrated that the multiple π - π stacking interactions due to the peripheral DMIP motifs are the key contributor in forming the self-assembled gel for dendritic gelator G_0G_2 -Me. To shed light on the driving forces in gel phase aggregation from the view point of a structure-property relationship study, single crystals of G_0G_1 dendrons with different peripheral ester groups and dendron skeleton, including G₀G₁-Me, 3-G₀G₁-Me, 4-G₀G₁-Me, 3,4-G₀G₁-Me, G_0G_1 -Et, and G_0G_1 '-Me were acquired through slow evaporation of acetonitrile/methanol mixed solutions at room temperature (see the Supporting Information), and the molecular structures were determined unambiguously by using X-ray crystallography analysis. From the packing analysis of the single crystals as shown in Figure S15 (the Supporting Information) and Figure 4, several intriguing features were noticed and summarized as follows: 1) The formation of extended coplanar π -systems of the peripherally ester-functionalized phenyl rings, consisting of a phenyl ring and C=O double bond, is essential for π - π stacking interactions. Although differing in composition and size, conjugated π -systems were observed in most crystal structures, except for 3,4-G₀G₁-Me, which could not form gel in all selected solvents; 2) At least one type of intermolecular π - π stacking interactions between two intermolecular peripheral extended π -systems was commonly observed for most single crystals, except for $4-G_0G_1-Me$, which is crucial for efficient gel formation; 3) Besides π - π stacking, intermolecular weak C–H··· π interactions (2.81–2.90 Å) and non-conventional hydrogen bonding (2.31-2.71 Å) were ubiquitous in all crystal structures. The hydrogen atoms of CH₃ or CH₂ of ester groups, different benzyl hydrogens, and phenyl hydrogens of all dendron layers could be hydrogen donors, whereas carbonyl oxygen atoms, benzyl oxygen atoms, and even the alcoholic oxygen atoms of ester groups could be acceptors for hydrogen bonding. At the same time, the π -systems involved in the C-H··· π interactions could be any substituted phenyl rings at the periphery or in the middle layer of the dendrons.

For the best gelator analogue G_0G_1 -Me, it was noted that two types of peripheral extended π -systems existed. For one of the two peripheral substituted phenyl rings in the molecule, both carbonyl groups were coplanar with the phenyl ring, and constituted a conjugated π -system. The two carbonyl oxygen atoms pointed outside, forming cooperative hydrogen-bonding interactions with the ortho hydrogen atom between the two ester groups. This peripheral DMIP ring (electron-deficient "head") was coplanar with the internal benzyl ring (electronrich "tail"). The two neighboring extended planes were stacked in head-to-tail pairs with interplanar distances of about 3.42 Å (Figure S15, the Supporting Information) indicative of π - π interactions. In the case of the other peripheral phenyl ring, the directions of the two carbonyls were opposite, but the coplanar extended π -system was still constructed including the phenyl ring and both the carboxylates. This peripheral DMIP ring adopted the "J-aggregation" π - π interaction mode with another peripheral DMIP ring of the same type in another dendron molecule with interplanar distances of about 3.42 Å. So, both peripheral DMIP rings and the internal phenyl ring all participate in the π - π stacking interactions, and compact lamellar aggregation of dendrons dominated by π - π interactions with the assistance of multiple intermolecular weak C–H··· π interactions (2.59–2.87 Å) between methyl groups of peripheral esters and DMIP rings and multiple non-conventional hydrogenbonding interactions related to the carbonyl oxygen atoms of the peripheral ester groups (2.42-2.71 Å) explains why peripherally DMIP-functionalized dendrons are the most effective in gel formation (Figure S15, the Supporting Information).

In the crystal structures of **3-G**₀**G**₁-**Me** and **4-G**₀**G**₁-**Me**, only one of the two peripheral ester-functionalized phenyl rings formed carbonyl conjugated π -systems. "*J*-aggregation" π - π interactions (3.60 and 3.70 Å) between these extended π -systems were observed for **3-G**₀**G**₁-**Me**, whereas instead, only multiple sets of CH··· π interactions (2.82–2.90 Å) were found in the crystal structure of **4-G**₀**G**₁-**Me**. For dendron **3,4-G**₀**G**₁-**Me**, whose analogue **3,4-G**₀**G**₂-**Me** could not form a gel in all of the



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Figure 4. Molecular structure and interactions of A) 3-G₀G₁-Me, B) 4-G₀G₁-Me, C) G₀G₁-Et, D) 3,4-G₀G₁-Me, and E) G₀G₁'-Me in single crystals.

selected solvents, no coplanar extended $\pi\text{-system}$ was observed but weak $\pi\text{-}\pi$ stacking and CH… π interactions were

found to exist in the crystal structure. In contrast with the two types of extended π -systems found in G_0G_1 -Me, only one of



the peripheral ester-functionalized phenyl rings of G0G1-Et formed carbonyl conjugated π -systems with the two carbonyl groups adopting an "opposite" conformation, and "J-aggregation" $\pi - \pi$ interactions (3.43 Å) between the same type of extended π -systems were proven to exist. In addition, two types of peripheral extended π -systems similar to those found in G_0G_1 -Me were also observed in the crystal structure of G_0G_1' -**Me**. Three kinds of π - π stacking interactions between peripheral extended π -systems were distinctly observed for **G**₀**G**₁'-**Me**, including two types of "H-aggregation" π - π stacking (3.28 and 3.43 Å) between the same π -systems and one type of "J-aggregation" π - π stacking (3.30 Å) between different π -systems. The internal phenyl ring was not involved in π - π stacking, differing from that found in the crystal structure of **G**₀**G**₁-**Me**. Such multiple π - π stacking interactions well explain the similar gelation properties exhibited by G_0G_1 - Me and G_0G_1 - Me. Relating the $\pi\text{-}\pi$ stacking interactions noted in different dendron crystal structures with their gelation abilities, it seems that highly efficient π - π stacking interactions of peripheral enlarged π -systems result in compact lamellar stacking of dendrons, thus play the most important role in the highly ordered self-assembly of these peripherally aromatic ester-functionalized dendrons.

Although the solvophobic effect may be the most conceivable motive for gel formation, the cooperative effects of multiple intermolecular and intramolecular non-covalent interactions, including various $\pi - \pi$ stacking, C–H··· π interactions, and hydrogen bonding, are responsible for the highly ordered and efficient self-assembly of these specific dendrons. For 3-G₀G₁-Me and G₀G₁-Et, one of the peripheral phenyl rings is enlisted in the π - π stacking, whereas the other peripheral phenyl ring usually participates in the C–H··· π interactions and/or hydrogen bonding. For G_0G_1 -Me and G_0G_1 '-Me, both peripherally ester-substituted phenyl rings participated in multiple π - π stacking, meanwhile, C–H··· π interactions and hydrogen bonding were also related to these peripheral aryl groups. Generally, most parts of the dendritic molecule were involved in the molecular-recognition process in a cooperative manner, which probably is the conceivable reason why these peripherally ester-functionalized poly(benzyl ether) dendrons without any conventional gelation motifs become efficient gelators in organic solvents, and why the dendritic structure has a high tolerance for gelation. Of course, the flexible molecular skeleton and versatile functionalities of the dendritic molecules are beneficial for the management of all these supramolecular recognitions to form gel phase material in the presence of plentiful solvent molecules. In conclusion, these peripherally multiple aromatic ester-functionalized poly(benzyl ether) dendrons are a new kind of dendritic gelators whose gel phase assembling is dominated by multiple π - π stacking interactions and cooperative C–H··· π interactions and hydrogen bonding due to the functionalized peripheral groups.

In addition to the single crystal structures, the π - π stacking interactions were further evidenced by powder X-ray diffraction (PXRD) studies.^[17,23] In the PXRD patterns of dendron xerogels of **G**₀**G**₁-**Me**, **G**₀**G**₁'-**Me**, and **G**₀**G**₁-**Et** from benzene (Figure S16, the Supporting Information), distinctive peaks at 2θ =

25.4, 24.4, and 25.2°, corresponding to a *d*-spacing of 3.50, 3.64, and 3.54 Å, respectively, were observed, suggesting typical π - π stacking interactions. In contrast, no apparent signal indicative for π - π stacking was found for xerogels of dendrons **4-G**₀**G**₁-**Me** and **3,4-G**₀**G**₁-**Me** (Figure S16, the Supporting Information).

¹H NMR spectroscopic studies in the sol and gel states

To further investigate the role of π - π stacking in gelation process, the molecular aggregation behaviors of G_0G_1 dendritic derivatives, including G₀G₁-Me, G₀G₁'-Me, 3-G₀G₁-Me, 4-G₀G₁-Me, 3,4-G₀G₁-Me, and G₀G₁-Et, in solution were confirmed by concentration-dependent (CD) and temperature-dependent (TD) ¹H NMR spectroscopy studies.^[17,24] In the CD-¹H NMR experiments in CD₃CN (Figure 5), the increase in solution concentration from 0.13 to 100 mm resulted in slight upfield shifts of the resonance signals for the aromatic protons on the peripheral ester-substituted phenyl rings (H(a) and H(b)) and the internal benzyl rings (H(c) and H(d)) for most dendrons tested, indicating crescent π - π stacking induced by molecular aggregation, except for $3,4-G_0G_1-Me$ (no extended conjugated π system was observed in its crystal structure). For example, the resonance signal of the aromatic proton H(a) on the peripheral phenyl rings of dendron G_0G_1 -Me showed the largest upfield shift ($\Delta \delta = 0.097$ ppm), whereas dendrons **G**₀**G**₁'-**Me**, **G**₀**G**₁-**Et**, 3-G₀G₁-Me, and 4-G₀G₁-Me gave upfield chemical shifts of Ha as $\Delta\delta$ = 0.063, 0.084, 0.016, and 0.020 ppm, respectively. A negligible upfield chemical shift of $\Delta \delta = 0.006$ ppm was noticed for dendron **3,4-G₀G₁-Me**, showing quite weak π - π stacking. In addition, the resonance signals of all the benzyl protons (H(h) and H(i)) were also found slightly upfield shifted in the experiments. It should be also noted that obvious peak broadening was observed for dendron G_0G_1 '-Me as the concentration increased to higher than 14.3 mm. So, π - π stacking interactions are proven universally existent in the solution phase aggregation of the peripherally aromatic ester-functionalized poly(benzyl ether) dendritic gelators.

TD-¹H NMR studies of G_0G_1 -Me in solution (CD₃CN, 14.3 mm) and G_0G_2 -Me in the gel state (CD₃CN, 8 mg mL⁻¹) were also carried out separately. Regarding the TD-¹H NMR experiments of G_0G_1 -Me in solution, the resonance signals related to the aromatic protons (H(a), H(b), H(c), and H(d)) were found to gradually shift downfield when the temperature increased from 10 to 55°C (Figure S18, the Supporting Information), indicating the weakening of π - π stacking. Notably, the signals corresponding to the benzyl ring at the focal point remained constant. A similar signal-shift trend was also observed in the gelsol phase transition experiments of G_0G_2 -Me upon warming from 20 to 90 °C (Figure S19, the Supporting Information). In addition to the downfield shifts of the related aromatic signals, all proton signals experienced a dramatic broadening below 50 °C, which is consistent with the virtually steady gel being retained under these conditions.

Based on all the above experimental evidences, multiple π - π stacking interactions, together with hydrogen bonding, C-H… π interactions, and solvophobic interactions might be the



H(a)

8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2

A

H(g)

H(b)

H(f) H(e)

H(b) COOMe

H(d)

G₀G₁-Me

H(c)

H(a)

COOMe

COOMe

COOMe

H(e) H(f) H(g)

0.13 mM 0.52 mM 1.64 mM 3.22 mM 7.69 mM 14.3 mM 33.3 mM 66.6 mM 100 mM

7.1 ppm



0.13 mM	H(d) H(e)	H(h+b) H(g) H(i)	H(a+c)				
0.52 mM	m	M	M				
1.64 mM		_n.M.m_					
3.22 mM		Mh_m	N				
7.69 mM		_MMm_					
14.3 mM		Mm					
33.3 mM		Mm	M				
66.6 mM		Mm_	N				
100 mM	//	Mm_					
7.1 ppm	7.4 7.3 7	7.6 7.5	7.8 7.7	7.9	8.0	8.1	8.2



0.13 mM	H(b') H(b)H(d)	H(e) H(f) H(g)	H(a)	
0.52 mM		MMm		
1.64 mM	_M_	MMm		
3.22 mM	LNL	MMm		
7.69 mM	_M_	MMm	<u>II</u>	
14.3 mM		MMm		
33.3 mM	_M_	M.h.m	M	
66.6 mM		Mm	M	
100 m M	_IML	MMm	l	
7.1 ppm	4 7.3 7.2	7.6 7.5 7.	8.1 8.0 7.9 7.8	8.2 8.







M		MM	1.64 mM
		M_	3.22 mM
		MM	7.69 mM
		MM	14.3 mM
N		M	33.3 mM
M		MM	
M		MMm	
8.2 8.1 8	0 7.9 7.8 7.7	7.6 7.5 7.4	7.3 7.2 7.1 ppm



			H(b)								
H(a)			1_			H(e)	H(f) H	(g)	H(c)	H(d)	0.13 mM
Λ							M	^		_/	0.52 mM
_/			Ĺ					·			1.64 mM
_/			_!_					~			3.22 mM
_/								~		_/	7.69 mM
_/			Ĺ					~	^		14.3 mM
						N	_m_	^- <u> </u>	^	_/_	33.3 mM
				Ļ			r.m.	~		r	66.6 mM
							nm				100 mM
8.2	8.1	8.0	7.9	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1 ppm

Figure 5. Partial ¹H NMR spectra (600 MHz, [D₃]CH₃CN) of dendrons at different concentrations (298 K) showing the aromatic region (using TMS as the internal standard): A) G₀G₁-Me, B) 3-G₀G₁-Me, C) 4-G₀G₁-Me, D) 3,4-G₀G₁-Me, E) G₀G₁-Et, F) G₀G₁'-Me.

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main contributors for the unique gelation capability of these peripherally aromatic ester-functionalized poly(benzyl ether) dendrons without bearing any conventional gelation motifs. Furthermore, the dendritic periphery dominated self-assembly of these poly(benzyl ether) dendrons in the gel phase renders them new dendritic gelation "motifs" awaiting further applications in the field of nanomaterials.

Thixotropic-responsive properties of the dendritic organogels

Thixotropic gels, which exhibit reversible sol-gel transformations upon exposure to external mechanical stress, represent an intriguing class of truly dynamic self-assembled supramolecular systems. Among hundreds of functional low-molecularweight gelators (LMWG) reported to date, only very few of them exhibited unique thixotropic properties.^[25] Containing multiple "adhesive termini" for non-covalent binding, dendritic gelators are envisioned to be superior in thixotropic materials than LMWG. However, only a few examples of thixotropic dendritic organogels have been reported so far.^[26] Therefore, it remains a great challenge to discover new dendritic organogel systems possessing thixotropic and self-repairing properties. Very excitingly, in the investigations of our peripherally multiple aromatic ester-functionalized poly(benzyl ether) dendritic gels, it was unexpectedly observed that the dendritic gels of G₀G₃-Me and G₀G₂-Me, formed in most solvents tested, exhibited thixotropic properties (Table S8, the Supporting Information). As shown in Figure 6, when treated with external me-



Figure 6. Photographs of the G_0G_3 -Me/1,2-dichloroethane gel (6 mM) upon mechanical stress: A) original gel before mechanical stress; B) The solution obtained after mechanical stress; C) The gel recovered upon resting for 1 h.

chanical stress, the translucent G_0G_3 -Me gel from 1,2-dichloroethane lost most of its viscosity and transformed into a viscous solution. After resting for at least 1 h at room temperature, the gel could be recovered. This cycling process could be repeated many times.

To verify the thixotropic behaviors of the dendritic organogels, rheological experiments were carried out with G_0G_3 -Me and G_0G_2 -Me gels. As shown in Figure 7 A, the storage modulus (G') and loss modulus (G'') as a function of angular frequency (ω) of the gel G_0G_3 -Me/1,2-dichloroethane at different concentrations were determined, showing that the gel behaved as a true gel. Strain amplitude sweeps were also proceeded to reveal the elastic response of the G_0G_3 -Me/1,2-dichloroethane gel (6 mM). As shown in Figure 7 B, the value of G' rapidly decreased in the region above the critical strain value ($\gamma > 1$ %), known as the upper of the linear viscoelastic regime, representing a partial collapse of the gel to a quasi-liquid state. Interestingly, this gel exhibited a very quick recovery of mechanical strength after the large amplitude oscillatory breakdown (Figure 7 C). For example, the initial value of G' was about 12500 Pa; it dropped to 64 Pa under a large amplitude oscillatory force ($\gamma = 100$ %; $\omega = 6.28$ rad s⁻¹ (1.0 Hz)), indicating the transformation to a quasi-liquid state. However, when the amplitude oscillation was decreased ($\gamma = 0.05\%$) at the same frequency (1.0 Hz), G' immediately recovered to about 80% of its initial value (9900 Pa) within 10 s, representing the recovery of a quasi-solid state. However, with prolonged time of more than one hour, G' and G'' could reach their initial values (Figure 7D). Furthermore, this thixotropic process could be repeated several times. The thixotropic properties of dendritic organogels of other generations (G₀G₂-Me) and/or in different solvents have also been investigated (Figure S20-S30 in the Supporting Information), affording conformable conclusions. All these results of rheological experiments indicate that G₀G₃-Me and **G**₀**G**₂-**Me** are promising candidates for thixotropic soft materials with both large mechanical strength and a fast recovery ability.

Conclusion

A series of peripherally aromatic ester-functionalized poly(benzyl ether) dendritic gelators with structural variations in focal point substitution, surface groups, dendron generations, and dendritic skeleton configuration have been synthesized. A systematic study of the structure–property relationships of these dendritic gelators, accompanied by the mechanism study by using XRD and CD-/TD-¹H NMR spectroscopic techniques, afford some important conclusions, which are useful for the molecular design of new dendritic gelators in the future:^[27]

- The gelation efficiency is highly dependent on the peripheral ester groups, not only through tuning the molecular solubility, but also by affecting the self-assembly mode; dendrons with DMIP motifs as peripheral layers turned out to be the most efficient gelators.
- 2) The generation effect of dendrons on gelation properties is clearly demonstrated although it is complicated. The gelation ability, the thermotropic behavior, the morphological properties, and even the rheological behavior vary upon an increase in generation.
- 3) The attachment of Fréchet dendrons at the focal point does not change the fact of stable gel formation for codendrimers G_mG_2 -Me, but the bigger the dendritic wedge, the worse the gelation ability.
- 4) The symmetric monodisperse dendritic skeleton is much more in favor of constructing highly efficient gel systems compared with the linear analogue and dissymmetric dendrons.
- 5) The multiple π - π stacking of extended π -systems due to the peripheral ester-functionalized phenyl rings, cooperatively assisted by supplementary intermolecular C-H··· π interactions and non-conventional hydrogen bonding, is the



Figure 7. Rheological data of G_0G_3 -Me gel from 1,2-dichloroethane (15 °C): A) Frequency sweeps ($\omega = 0.1-100 \text{ rad s}^{-1}$) at different concentrations (c = 4, 6, 8, and 10 mm); B) Strain amplitude sweeps; C) Step strain; D) Time sweep measurement (c = 6 mm). Step strain was a continuous measurement for four cycles.

key contributor in the formation of stable self-assembled gels, which is supported firmly by single-crystal XRD analysis and CD-/TD-¹H NMR spectroscopy in solution and in the gel state.

6) Furthermore, these dendritic organogelators were found to exhibit unexpected multiple stimuli-responsive behaviors upon exposure to environmental stimuli,^[26,28] such as temperature and mechanical stress, which makes them a new kind of dendritic candidates with potential applications in the field of intelligent soft materials.

In summary, we have demonstrated that the peripherally multiple aromatic ester, in particular, DMIP-functionalized, poly-(benzyl ether) dendrons are a new class of efficient dendritic organogelators. Distinguished from the core- and skeletonfunctionalized dendritic gelators, for example, dendrons bearing amide groups at the core or skeleton backbone, our dendritic gelators are functionalized at the periphery, whose gelphase self-assembly is dominated by synergistic non-covalent interactions due to the peripheral ester-functionalized benzyl rings, instead of the conventional gelation motifs like long alkyl chains or steroidal groups, leaving the focal point vacant to facilitate post-functionalization. Furthermore, these gelators can tolerate a bulky substituent at the core, which renders them efficient dendritic gelation motifs and provides a great opportunity for incorporating a functional group into the core to fabricate functional supramolecular materials.^[20] These discoveries thus open up a new avenue for the rational design of new types of dendritic gelators and corresponding functional soft materials.^[27]

Experimental Section

General

All chemicals were obtained from Aldrich, Alfa, or Acros and used as received unless otherwise mentioned. The organic solvents used were dried according to published methods. Unless otherwise noted, all reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AMX 300 Spectrometer (¹H: 300 MHz; ¹³C: 75 MHz) or Bruker AMX-600 spectrometers (¹H: 600 MHz; ¹³C: 150 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm) relative to the internal standards, partially deuterated solvents or tetramethylsilane (TMS). Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br =

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broad. Matrix-assisted laser desorption-ionization (time of flight) mass spectrometry (MALDI-TOF) was performed on a Bruker Biflex III MALDI-TOF spectrometer with α -cyano-4-hydroxylcinnamic acid (CCA) as the matrix. HRMS-FAB spectra were performed on a Bruker APEX 47E FTMS spectrometer. HRMS-ESI mass spectra were obtained on a Bruker APEX IV instrument. Elemental analyses were performed on a Carlo–Erba-1106 instrument.

Scanning electron microscopy (SEM)

The morphologies and sizes of the dendron xerogels were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an accelerating voltage of 15 kV. Samples were prepared by drop casting the suspension of freeze-dried gel in hexane on a silicon substrate. To minimize sample charging, a thin layer of Au was deposited onto the samples before SEM examination.

Environmental scanning electron microscopy (ESEM)

The morphologies and sizes of the dendron xerogels were characterized by FEI Quanta 200 ESEM FEG at an accelerating voltage of 10 kV. Samples were prepared by drop-casting the suspension of freeze-dried gel in hexane on a silicon substrate.

Transmission electron microscopy (TEM)

TEM was performed on a JEOL JEM-2011 and JEOL JEM-1011 microscope. Samples were prepared by drop-casting the suspension of freeze-dried gel in hexane on carbon-coated copper grids and the TEM pictures were obtained without staining.

Single-crystal X-ray diffraction

A crystal suitable for X-ray diffraction was obtained by slow evaporation of dendron solution at room temperature. All data were collected on a Rigaku Saturn X-ray diffractometer with graphite-monochromator $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 113 K. Intensities were collected for absorption effects by using the multi-scan technique SADABS. The structures were solved by direction methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program (Sheldrick, 1997). The extended packing plots and data from crystal packing were obtained by using the software Mercury 1.4.1. CCDC-980756 (G_0G_1 -Me), CCDC-980757 ($3-G_0G_1$ -Me), CCDC-980758 ($4-G_0G_1$ -Me), CCDC-980759 ($3,4-G_0G_1$ -Me), CCDC-980760 (G_0G_1 -Et), and 980761 (G_0G_1' -Me) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction (PXRD)

The gel of the dendron in benzene was coated on a glass plate and the solvent was slowly evaporated. Then, the glass plates with dry gels were fixed on a sample holder and subjected to XRD analysis at room temperature on a Japan Rigaku D/MAX-2500/PC diffractometer. XRD patterns were recorded at a scanning rate of 2° min⁻¹ in the 2θ range of 0.5 to 30 with Cu_{Ka} radiation (λ = 1.54178 Å).

Rheological measurements

Rheological measurements were carried out with a stress-controlled rheometer (TA Instruments, $AR-G_2$) equipped with steel parallel-plate geometry (40 mm diameter). The gap distance was fixed at 750 μ m. A solvent-trapping device was placed above the plate to avoid evaporation. When gel samples were mounted on the plate, they were allowed to stand for at least 5 min to facilitate the recovery of the structure. All measurements were made at 15 or 20°C. A strain sweep at a constant frequency (6.28 rad s⁻¹) was performed in the 0.01–200% range to determine the linear viscoelastic region (LVER) of the gel sample. The frequency sweep was obtained from 0.1 to 100 rad s^{-1} at a constant strain of 0.03 or 0.05 %, well within the linear regime determined by the strain sweep. A thixotropic study was conducted to examine the recovery behavior of dendritic organogels after the strain sweep. The recovery of the storage modulus of the destroyed gel is monitored at a constant frequency (6.28 rad s⁻¹) under a low strain (0.05%) just after the strain sweep progress. The storage modulus G' and the loss modulus G" are recorded as functions of time in the recovery process. To investigate the recovery properties of the samples in response to applied shear forces, we used the following programmed procedure (applied shear force, expressed in terms of strain; duration in parentheses): 1) Standing the gel sample for 5 min after mounting; 2) Linear small-amplitude oscillations (at $\gamma = 0.05\%$ and $\omega = 1$ Hz) for 5 min to monitor initial value of G' and G''; 3) Nonlinear, largeamplitude oscillations ($\gamma = 100\%$) at the same frequency for 1.5 min to break down the gel structure; 4) Linear small-amplitude oscillations ($\gamma = 0.05\%$) for 5 min at the same frequency to monitor recovery of mechanical strength of gels; 5) An additional two cycles of the breakdown and recovering processes described in (3) and (4). The measurements were carried out with the solvent-trap to prevent drying a gel sample during the long-time measurement. The storage modulus G' and the loss modulus G'' are recorded as functions of time in both processes.

Gelation test

A weighed sample of a dendritic organogelator was mixed with selected solvent (0.5 mL) in a septum-capped vial and heated in an oil bath until the solid was dissolved. Then, the sample vial was cooled to room temperature. The aggregation state was then assessed. If no flow was observed when inverting the vial, a stable gel was formed and noted as gelation (G). If part of the mixture formed a gel but flow was still observed, the phenomenon was recorded as partial gelation (PG). If precipitation occurred, P was noted, and if the clear solution (>60 mg mL⁻¹) was retained, it was marked as soluble (S). If the compound was unable to dissolve, it was noted as insoluble (I). In some solvent systems (for example, 2methoxyethanol, acetonitrile), short-term sonication (0.40 W cm⁻², 40 KHz, 1-2 min) was required at the beginning of the cooling process. Repeated heating and cooling confirmed the thermoreversibility of the gelation process. The critical gelation concentration (CGC) of the organogelator was determined by measuring the minimum amount of gelator required for the formation of a stable gel at room temperature.

Acknowledgements

The authors thank the National Natural Science Foundation of China (No 21074140 and 91027046) and the National Basic Research Program of China (973 program, No. 2013CB932800) for financial support.

Keywords: dendrimers · gelators · organogels · self-assembly · structure–property relationships

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- [1] For selected reviews, see: a) Molecular Gels: Materials with Self-Assembled Fibrillar Networks (Eds.: R. G. Weiss, P. Terech), Springer, Amsterdam, 2006; b) Functional Molecular Gels (Eds.: B. Escuder, J. F. Miravet), The Royal Society of Chemistry, Cambridge, 2014; c) R. G. Weiss, Langmuir 2009, 25, 8369–8369, and reviews from this special issue; d) P. Terech, R. G. Weiss, Chem. Rev. 1997, 97, 3133–3160; e) N. M. Sangeetha, U. Maitra, Chem. Soc. Rev. 2005, 34, 821–836; f) P. Dastidar, Chem. Soc. Rev. 2008, 37, 2699–2715; g) M. O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, Chem. Rev. 2010, 110, 1960–2004; h) A. Dawn, T. Shiraki, S. Haraguchi, S. Tamaru, S. Shinkai, Chem. Asian J. 2011, 6, 266–282; i) A. Y. Y. Tam, V. W. W. Yam, Chem. Soc. Rev. 2013, 42, 1540–1567; j) G. C. Yu, X. Z. Yan, C. Y. Han, F. H. Huang, Chem. Soc. Rev. 2013, 42, 6697–6722; k) K. K. Kartha, R. D. Mukhopadhyay, A. Ajayaghosh, Chimia 2013, 67, 51–63; i) S. S. Babu, V. K. Praveen, A. Ajayaghosh, Chem. Rev. 2014, 114, 1973–2129.
- [2] For recent reviews, see: a) A. R. Hirst, D. K. Smith, *Top. Curr. Chem.* 2005, 256, 237–273; b) D. K. Smith, *Adv. Mater.* 2006, 18, 2773–2778; c) D. K. Smith, *Chem. Commun.* 2006, 34–44.
- [3] a) G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z. Q. Yao, J. E. Miller, K. Bouillion, J. Chem. Soc. Chem. Commun. 1986, 752–753; b) G. R. Newkome, G. R. Baker, S. Arai, M. J. Saunders, P. S. Russo, K. J. Theriot, C. N. Moorefield, L. E. Rogers, J. E. Miller, T. R. Lieux, M. E. Murray, B. Phillips, L. Pascal, J. Am. Chem. Soc. 1990, 112, 8458–8465; c) G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamilla, M. J. Saunders, Angew. Chem. 1992, 104, 901–903; Angew. Chem. Int. Ed. Engl. 1992, 31, 917–919.
- [4] a) C. Marmillon, F. Gauffre, T. Gulik-Krzywicki, C. Loup, A. M. Caminade, J. P. Majoral, J. P. Vors, E. Rump, Angew. Chem. 2001, 113, 2696–2699; Angew. Chem. Int. Ed. 2001, 40, 2626–2629; b) A. El Ghzaoui, F. Gauffre, A. M. Caminade, J. P. Majoral, H. Lannibois-Drean, Langmuir 2004, 20, 9348–9353; c) C. Kojima, S. Tsumura, A. Harada, K. Kono, J. Am. Chem. Soc. 2009, 131, 6052–6053; d) Q. G. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara, T. Aida, Nature 2010, 463, 339–343.
- [5] a) W. D. Jang, D. L. Jiang, T. Aida, J. Am. Chem. Soc. 2000, 122, 3232–3233; b) W. D. Jang, T. Aida, Macromolecules 2003, 36, 8461–8469.
- [6] a) C. Kim, K. T. Kim, Y. Chang, H. H. Song, T. Y. Cho, H. J. Jeon, J. Am. Chem. Soc. 2001, 123, 5586–5587; b) C. Kim, S. J. Lee, I. H. Lee, K. T. Kim, H. H. Song, H. J. Jeon, Chem. Mater. 2003, 15, 3638–3642; c) J. Lee, J. M. Kim, M. Yun, C. Park, J. Park, K. H. Lee, C. Kim, Soft Matter 2011, 7, 9021–9026.
- [7] a) K. S. Partridge, D. K. Smith, G. M. Dykes, P. T. McGrail, *Chem. Commun.* 2001, 319–320; b) A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts, A. C. Wright, *J. Am. Chem. Soc.* 2003, *125*, 9010–9011; c) B. Q. Huang, A. R. Hirst, D. K. Smith, V. Castelletto, I. W. Hamley, *J. Am. Chem. Soc.* 2005, *127*, 7130–7139; d) A. R. Hirst, J. F. Miravet, B. Escuder, L. Noirez, V. Castelletto, I. W. Hamley, D. K. Smith, *Chem. Soc.* 2013, *135*, 5911–5920.
- [8] a) Y. Ji, Y. F. Luo, X. R. Jia, E. Q. Chen, Y. Huang, C. Ye, B. B. Wang, Q. F. Zhou, Y. Wei, *Angew. Chem.* 2005, *117*, 6179–6183; *Angew. Chem. Int. Ed.* 2005, *44*, 6025–6029; b) G. C. Kuang, Y. Ji, X. R. Jia, E. Q. Chen, M. Gao, J. M. Yeh, Y. Wei, *Chem. Mater.* 2009, *21*, 456–462; c) G. C. Kuang, X. R. Jia, M. J. Teng, E. Q. Chen, W. S. Li, Y. Ji, *Chem. Mater.* 2012, *24*, 71–80.
- [9] a) H. F. Chow, J. Zhang, *Chem. Eur. J.* 2005, *11*, 5817–5831; b) K. N. Lau,
 H. F. Chow, M. C. Chan, K. W. Wong, *Angew. Chem.* 2008, *120*, 7018–7022; *Angew. Chem. Int. Ed.* 2008, *47*, 6912–6916.
- [10] M. Yang, Z. J. Zhang, F. Yuan, W. Wang, S. Hess, K. Lienkamp, I. Lieberwirth, G. Wegner, *Chem. Eur. J.* 2008, 14, 3330–3337.
- [11] a) P. F. Duan, M. H. Liu, *Langmuir* **2009**, *25*, 8706–8713; b) P. F. Duan, L. Qin, X. F. Zhu, M. H. Liu, *Chem. Eur. J.* **2011**, *17*, 6389–6395; c) L. Qin, P. F. Duan, F. Xie, L. Zhang, M. H. Liu, *Chem. Commun.* **2013**, *49*, 10823–10825.
- [12] a) E. R. Zubarev, M. U. Pralle, E. D. Sone, S. I. Stupp, J. Am. Chem. Soc.
 2001, 123, 4105-4106; b) E. R. Zubarev, E. D. Sone, S. I. Stupp, Chem. Eur. J. 2006, 12, 7313-7327.
- [13] M. Yoshida, Z. M. Fresco, S. Ohnishi, J. M. J. Fréchet, *Macromolecules* **2005**, *38*, 334–344.
- [14] M. Seo, J. H. Kim, J. Kim, N. Park, J. Park, S. Y. Kim, Chem. Eur. J. 2010, 16, 2427–2441.

- [15] a) X. C. Yang, R. Lu, F. Y. Gai, P. C. Xue, Y. Zhan, *Chem. Commun.* **2010**, *46*, 1088–1090; b) Z. C. Ding, R. B. Xing, X. D. Wang, J. Q. Ding, L. X. Wang, Y. C. Han, *Soft Matter* **2013**, *9*, 10404–10412.
- [16] A. Pérez, J. L. Serrano, T. Sierra, A. Ballesteros, D. Saá, J. Barluenga, J. Am. Chem. Soc. 2011, 133, 8110–8113.
- [17] Y. Feng, Z. T. Liu, J. Liu, Y. M. He, Q. Y. Zheng, Q. H. Fan, J. Am. Chem. Soc. 2009, 131, 7950–7951.
- [18] Y. Feng, Y. M. He, L. W. Zhao, Y. Y. Huang, Q. H. Fan, Org. Lett. 2007, 9, 2261–2264.
- [19] A. R. Hirst, I. A. Coates, T. R. Boucheteau, J. F. Miravet, B. Escuder, V. Castelletto, I. W. Hamley, D. K. Smith, J. Am. Chem. Soc. 2008, 130, 9113– 9121.
- [20] a) Q. Chen, Y. Feng, D. Q. Zhang, G. X. Zhang, Q. H. Fan, S. N. Sun, D. B. Zhu, *Adv. Funct. Mater.* 2010, *20*, 36–42; b) Q. Chen, D. Q. Zhang, G. X. Zhang, X. Y. Yang, Y. Feng, Q. H. Fan, D. B. Zhu, *Adv. Funct. Mater.* 2010, *20*, 3244–3251; c) Z. X. Liu, Y. Feng, Z. C. Yan, Y. M. He, C. Y. Liu, Q. H. Fan, *Chem. Mater.* 2012, *24*, 3751–3757; d) X. Y. Yang, G. X. Zhang, L. Q. Li, D. Q. Zhang, L. F. Chi, D. B. Zhu, *Small* 2012, *8*, 578–584; e) G. Z. Zhao, L. J. Chen, W. Wang, J. Zhang, G. Yang, D. X. Wang, Y. H. Yu, H. B. Yang, *Chem. Eur. J.* 2013, *19*, 10094–10100; f) Z. X. Liu, Y. Feng, Z. Y. Zhao, Z. C. Yan, Y. M. He, X. J. Luo, C. Y. Liu, Q. H. Fan, *Chem. Eur. J.* 2014, *20*, 533–541.
- [21] a) S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* 2001, 101, 3819–3867;
 b) C. J. Hawker, J. M. J. Fréchet, *J. Chem. Soc. Chem. Commun.* 1990, 1010–1013; c) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* 1990, 112, 7638–7647; d) C. J. Hawker, J. M. J. Fréchet, *Macromolecules* 1990, 23, 4726–4729.
- [22] a) N. Mohmeyer, H. W. Schmidt, *Chem. Eur. J.* 2005, *11*, 863–872;
 b) D. M. Ryan, S. B. Anderson, B. L. Nilsson, *Soft Matter* 2010, *6*, 3220–3231.
- [23] a) A. Ajayaghosh, S. J. George, J. Am. Chem. Soc. 2001, 123, 5148-5149;
 b) J. Hu, D. Zhang, S. Jin, S. Z. D. Cheng, F. W. Harris, Chem. Mater. 2004, 16, 4912-4915.
- [24] a) T. Tu, W. Assenmacher, H. Peterlik, R. Weisbarth, M. Nieger, K. H. Dötz, *Angew. Chem.* 2007, 119, 6486–6490; *Angew. Chem. Int. Ed.* 2007, 46, 6368–6371; b) G. Fernández, L. Sánchez, E. M. Pérez, N. Martín, *J. Am. Chem. Soc.* 2008, 130, 10674–10683; c) W. Lu, Y. Law, J. Han, S. S. Chui, D. Ma, N. Zhu, C. M. Che, *Chem. Asian J.* 2008, 3, 59–69.
- [25] For selected examples, see: a) J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg, B. L. Feringa, Chem. Eur. J. 1999, 5, 937-950; b) P. Terech, D. Pasquier, V. Bordas, C. Rossat, Langmuir 2000, 16, 4485-4494; c) J. B. Beck, S. J. Rowan, J. Am. Chem. Soc. 2003, 125, 13922-13923; d) X. Huang, S. R. Raghavan, P. Terech, R. G. Weiss, J. Am. Chem. Soc. 2006, 128, 15341-15352; e) W. G. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowan, J. Am. Chem. Soc. 2006, 128, 11663-11672; f) J. Liu, P. L. He, J. L. Yan, X. H. Fang, J. X. Peng, K. Q. Liu, Y. Fang, Adv. Mater. 2008, 20, 2508-2511; g) P. Mukhopadhyay, N. Fujita, A. Takada, T. Kishida, M. Shirakawa, S. Shinkai, Angew. Chem. 2010, 122, 6482-6486; Angew. Chem. Int. Ed. 2010, 49, 6338-6342; h) T. D. Hamilton, D. K. Bucar, J. Baltrusaitis, D. R. Flanagan, Y. J. Li, S. Ghorai, A. V. Tivanski, L. R. MacGillivray, J. Am. Chem. Soc. 2011, 133, 3365-3371; i) A. Dawn, T. Shiraki, H. Ichikawa, A. Takada, Y. Takahashi, Y. Tsuchiya, L. T. N. Lien, S. Shinkai, J. Am. Chem. Soc. 2012, 134, 2161-2171; j) M. M. Zhang, D. H. Xu, X. Z. Yan, J. Z. Chen, S. Y. Dong, B. Zheng, F. H. Huang, Angew. Chem. 2012, 124, 7117 - 7121; Angew. Chem. Int. Ed. 2012, 51, 7011 - 7015.
- [26] a) V. Percec, M. Peterca, M. E. Yurchenko, J. G. Rudick, P. A. Heiney, *Chem. Eur. J.* **2008**, *14*, 909–918; b) J. Liu, Y. Feng, Z. X. Liu, Y. M. He, Q. H. Fan, *Chem. Asian J.* **2013**, *8*, 572–581.
- [27] Y. Feng, Z. X. Liu, L. Y. Wang, H. Chen, Y. M. He, Q. H. Fan, *Chin. Sci. Bull.* 2012, *57*, 4289–4295, and unpublished results.
- [28] a) Y. Ji, G. C. Kuang, X. R. Jia, E. Q. Chen, B. B. Wang, W. S. Li, Y. Wei, J. Lei, *Chem. Commun.* **2007**, 4233–4235; b) J. H. Kim, M. Seo, Y. J. Kim, S. Y. Kim, *Langmuir* **2009**, *25*, 1761–1766; c) G. C. Kuang, Y. Ji, X. R. Jia, Y. Li, E. Q. Chen, Z. X. Zhang, Y. Wei, *Tetrahedron* **2009**, *65*, 3496–3501; d) P. Rajamalli, E. Prasad, *Org. Lett.* **2011**, *13*, 3714–3717.

Received: January 14, 2014 Published online on April 17, 2014

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