

Two-Component Dendritic Gels: Easily Tunable Materials

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Over recent years, there has been an explosive growth of interest in the development of novel gel-phase materials based on small molecules.¹ It has been recognized that an effective gelator should possess functional groups that interact with each other via temporal associative forces. This process leads to the formation of supramolecular polymerlike structures,² which then aggregate further, hence gelling the solvent. Supramolecular interactions between building blocks that enable gel formation include hydrogen bonds, π - π interactions, solvophobic effects, and van der Waals forces.³ Recently, great emphasis has been placed on ways in which the structure of the gelator can control gel formation.⁴ This has led to the investigation of a wide range of structurally diverse gelators, including those with dendritic structures.⁵

In some cases, which are still relatively rare, two-component gelators have been reported.^{6–8} The two components interact with one another to form a complex, which is then capable of further self-assembly leading to gelation. In 2001, we reported the first dendritic two-component system for the gelation of organic solvents (Figure 1).⁹ This system has a number of features that are important for gel formation: (a) acid–base interactions between components (hydrogen bonds either with or without associated proton transfer), (b) dendritic branching, and (c) an aliphatic diamine spacer chain. This communication illustrates that using two components enhances the tunability of gel-phase materials and highlights three simple ways in which the macroscopic properties and microstructural features of these gels can be controlled.

As might be expected, the *concentration* of the gelator system controls the structure and properties of the gel. The solvated gelator network was observed using cryo scanning electron microscopy (cryo SEM) at different concentrations, maintaining a 2:1 dendrimer:diamine ratio. At low concentrations, thin fibers were present (Figure 2a), which at higher concentration aggregate and assemble into thick fiber bundles (Figure 2b). The effect of molar concentration on the *thermally reversible gel-sol phase transition* (T_{gel}) was monitored using the tube inversion technique.¹⁰ As the molar concentration of the two components was increased, T_{gel} also increased (Figure 2c). This mirrors the cryo SEM observations, in which, as would be expected, more concentrated samples form a more extensive network. Eventually, however, a plateau value of T_{gel} was obtained, indicating that once the molar concentration reaches a certain threshold (ca. 15 mM), the gelation of the solvent is effectively maximized.

In a two-component gel, it is easy to modify the *molecular structure* of either of the two components. Interestingly, decreasing the length of the aliphatic spacer chain had a remarkable effect on the T_{gel} values of the gels in the plateau region ($[1] > 15$ mM). T_{gel}

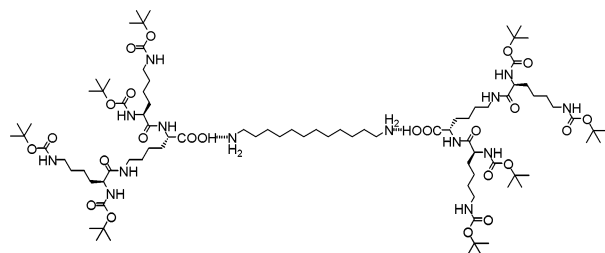


Figure 1. Structure of two-component gelation system **A** based on the interaction between dendritic branch **1** and diaminododecane **2**.¹⁰

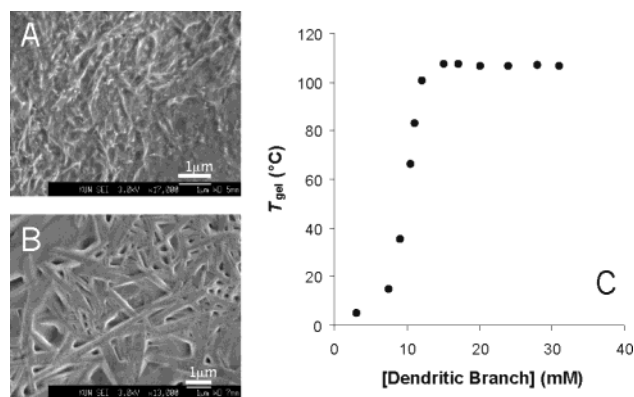


Figure 2. Effect of concentration on gel structure and thermal properties. (a) Cryo SEM of gelation system **A** in toluene: $[1] = 3$ mM, $[2] = 1.5$ mM. (b) Cryo SEM of gelation system **A** in toluene: $[1] = 10$ mM, $[2] = 5$ mM. (c) Effect of $[1]$ on the gel-sol transition temperature (T_{gel}) of the gel in toluene; all samples have a 2:1 dendrimer:diamine ratio.

decreased from 105 °C (C12) to 92 °C (C11) to 72 °C (C10) to 55 °C (C9) and to 41 °C (C8). This is one of the largest changes in T_{gel} that has been reported using simple structural modifications and indicates that T_{gel} can be dramatically tuned in this two-component system. van der Waals interactions between aliphatic chains may play a key role in mediating the assembly of the gel-phase network. Aromatic spacer chains have also been investigated, but the results thus far have shown poor reproducibility. Replacing the second-generation dendritic peptide with a first-generation analogue prevented gel formation at room temperature, indicating that the extent of branching also plays an important structural role: there is the possibility of branch–branch hydrogen bond interactions between amide groups.

Most interestingly, the *ratio of the two components* has a profound effect on the microscopic structure and macroscopic properties of the gel in toluene. SEM indicated that there was a dramatic change in morphology on tuning the ratio of the two components. Samples formed using a 2:1 dendrimer:diamine ratio possessed a *fibrous* microstructure (Figure 3a). When the diamine content was increased (1:4.5), however, flattened *platelets* with

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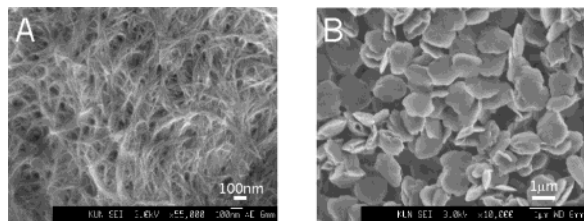


Figure 3. (a) SEM of a 2:1 dendrimer:diamine gelation system **A** in toluene: $[1] = 9$ mM, $[2] = 4.5$ mM. (b) SEM of a 1:4.5 dendrimer:diamine gelation system **A** in toluene: $[1] = 9$ mM, $[2] = 40.5$ mM.

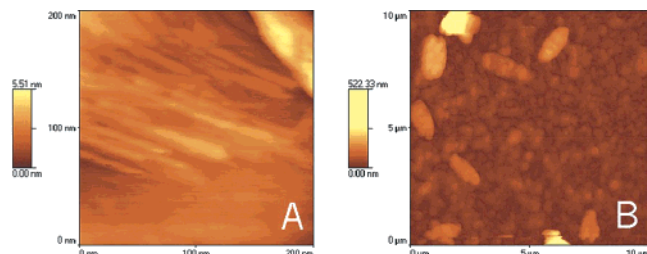


Figure 4. (a) AFM image of a 2:1 dendrimer:diamine gelation system **A** in toluene: $[1] = 0.3$ mM, $[2] = 0.15$ mM. (b) AFM image of a 1:4 dendrimer:diamine gelation system **A** in toluene: $[1] = 0.3$ mM, $[2] = 1.2$ mM.

diameters of approximately $1\ \mu\text{m}$ became the dominant motif (Figure 3b). At intermediate ratios, the structure changed from fibrous (1:1) to thick bundles of fibers (1:2.7) (see Supporting Information).

Interestingly, the gel-sol transition temperature, T_{gel} , was also strongly dependent on the ratio of the two components. The diamine-rich sample (1:4.5) would only form a gel-phase material when cooled below room temperature, while samples that were richer in dendrimer than a 1:4 ratio had T_{gel} values greater than $35\ ^\circ\text{C}$ and were all gels at room temperature. Intriguingly, this difference in macroscopic behavior reflects the different microscopic structures found by SEM and indicates that the platelet microstructure formed in the diamine-rich samples is a thermodynamically less stable network than the fibers formed when more dendritic branching is present.

The nature of the aggregates present below the gelation threshold concentration was then investigated using atomic force microscopy (AFM). When the two components were present in a 2:1 dendrimer:diamine ratio, rodlike aggregates were observed in the AFM images (Figure 4a shows aligned rods running from upper left to lower right). The length of these rods was approximately 100 nm, and their diameters were ca. 9 nm (depth = ca. 1 nm). When the two components were dissolved in a 1:4 dendrimer:diamine ratio, however, disklike structures were observed (Figure 4b). These disks had dimensions ($1\text{--}2\ \mu\text{m}$) very similar to the structures previously observed using SEM on the gel-phase materials. In addition, spheres of ca. 100 nm in diameter were observed by AFM. The different morphologies induced by changing the ratio of the two components are therefore observed using AFM, indicating that these structures are the fundamental building blocks of the macroscopic gel-phase network. To the best of our knowledge, this switching of aggregate morphology has not previously been observed in two-component gel-phase materials.

In none of the investigations were aggregates observed when only one of the two components was present, i.e., the presence of both components is essential for gel formation.

From the results presented in this paper, it is clear that the dendrimer:diamine ratio directly controls the microscopic structure, and, in turn, the macroscopic properties (T_{gel}) of the gel-phase material. This is the first time that such an effect has been delineated for a two-component gel and indicates the controllability of such systems. Furthermore, the ability of both the molecular structures of the two components and the concentration of the sample employed to control the T_{gel} endows these materials with considerable additional tunability. Our current and future work is focusing on investigations to yield further insight into the precise mode of assembly and the reasons behind the formation of different morphologies. We anticipate that this general two-component approach to gel formation will lead to a wide range of interesting materials with tunable microscopic and macroscopic properties and potentially interesting applications such as drug delivery.¹¹

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Supporting Information Available: Additional SEM images with intermediate dendrimer:diamine ratios and experimental protocols (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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