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Self-assembly of two-component peptidic dendrimers: dendritic effects on gel-phase materials

Andrew R. Hirst and David K. Smith*
Department of Chemistry, University of York, Heslington, York, UK YO10 5DD.
E-mail: dks3@york.ac.uk

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The self-assembly of diaminododecane solubilised by different dendritic peptides, possessing increasing levels of dendritic branching, was investigated. The dendritic peptides were based on L-lysine building blocks and were of first, second and third generation, containing one, three and seven amino acid repeat units respectively. By applying these structures as potential gelator units, the dendritic effect on gelation was investigated. The degree of structuring was modulated, with the dendritic peptide controlling the aggregate morphology and the ability of the self-assembled state to manifest itself macroscopically as gelation. First generation gelator units (**G1**) did not induce macroscopic gelation with diaminododecane under any conditions, whilst those self-assemblies based on second (**G2**) and third (**G3**) generation branches did form gel-phase materials. Furthermore, gel-phase materials based on **G2** exhibited optimum gelation behaviour compared to those based on **G3** (in terms of the thermal strength of the materials). Circular dichroism showed that the dendritic effect, programmed in at the molecular level, is directly related to the degree of chiral organisation within the self-assembled state. The dendritic generation of the peptide controls the pattern of amide–amide hydrogen bonding in terms of binding strength and alignment as determined using NMR methods. The mode of self-assembly can be qualitatively rationalised in terms of an attractive enthalpic interaction (*i.e.*, amide–amide hydrogen bonding), a repulsive interaction (*i.e.*, steric interactions between dendritic peptides) and an entropic term related to the hierarchical organisation of the gelator building blocks. It is argued that the balance between these factors determines the nature of the dendritic effect.

Introduction

Supramolecular chemistry investigates self-assembly as a consequence of the formation of non-covalent interactions (*i.e.*, hydrogen bonding, π–π stacking, solvophobic effects and van der Waals forces).[1] At this interface between chemistry, biology and materials science, it is interesting to understand the design principles that govern molecular self-assembly. One of the most exciting current frontiers of supramolecular chemistry is the self-assembly of multiple small molecule building blocks into one-dimensional fibrous structures, which are expressed on the macroscopic level as gel-phase materials.[2] Many different structures capable of acting as gelators have now been reported, however, a full predictive understanding of the assembly process is still elusive. On the other hand, different types of self-assembly, which have been investigated for a number of years, such as the self-assembly of surfactant molecules *are* well-understood. For the self-assembly of surfactant molecules in aqueous media, aggregation and morphological changes can be related to molecular parameters such as hydrophobic volume, chain length and head group volume, as well as intensive variables such as temperature and ionic strength.[3] Theories have been developed which predict the optimal mode of aggregation for a given set of variables. Of particular interest is the effect of head group volume, and in analogy to studies with surfactants, this paper considers the effect of differently sized head groups, but in this case on the assembly of gel-phase materials using dendritic building blocks.

Dendritic molecules capable of gelating organic solvents are a very recent development, and the effect of dendritic generation on the assembly process and the resultant gel-phase materials properties is somewhat ambiguous. In 2000, Aida and co-workers first reported a dendritic gelator for organic solvents, which operates at low concentrations (1% wt/vol).[4] Their dendron, based on Fréchet-type branching with a peptide at the focal point, required at least second generation branching to gelate organic solvents, however, no quantitative dendritic effect was determined. Simanek and co-workers reported dendritic gels based on triazines, but in this case, no clear dendritic effect on materials properties was observed.[5] Stupp and co-workers have also investigated the assembly of dendron rodcoils into supramolecular nanoribbons.[6] In this case, although different generations of dendron blocks have been used,[7] the optimum for assembly is a relatively small dendritic unit. Stupp and co-workers have also reported dendron substituted cholesteryl-(L-lactic acid) for self-assembly, and observed that the supramolecular organisation was dependent on the size of the dendritic head group.[8] Kim and co-workers have used peptidic dendrons to form gel-phase assembled materials at relatively high concentrations (8% wt/vol).[9] They observed a *negative* dendritic effect, with the gel–sol transition temperature (T_{gel}) decreasing with increasing dendritic generation. In contrast, we have recently investigated a one-component gelator in which L-lysine based dendritic branches (dendrons) were covalently coupled to cystamine dihydrochloride. In this case, a major *positive* dendritic effect was observed and quantified—increasing the extent of dendritic branching significantly enhanced the macroscopic T_{gel}.[10] There is currently no framework which can provide a predictive understanding of dendritic effects on gelation processes. This has inspired us to continue our experimental approach to determining the effects of the dendritic 'head group' size on the gelation process, in analogy to the effect of head group volume on surfactant assembly.

We have recently elucidated the basic design principles of a two-component gelator for aprotic organic solvents based on the interaction of dendritic building blocks with different aliphatic diamines (Fig. 1B).[11] We have clearly demonstrated that amide–amide hydrogen bonds between the dendritic head groups are the principal interactions which favour the self-assembly process—macroscopically expressed as gelation. We have found that the molecular information preset in the diamine modulates the transcription of chirality from the molecular to the mesoscopic level.[11d] Furthermore, we have also found that the individual stereocentres at the molecular level in the dendritic peptide directly control the self-assembly and the helicity within the fibrous aggregates.[11e] The chirality controls the pattern of hydrogen bonding within the meso-scale

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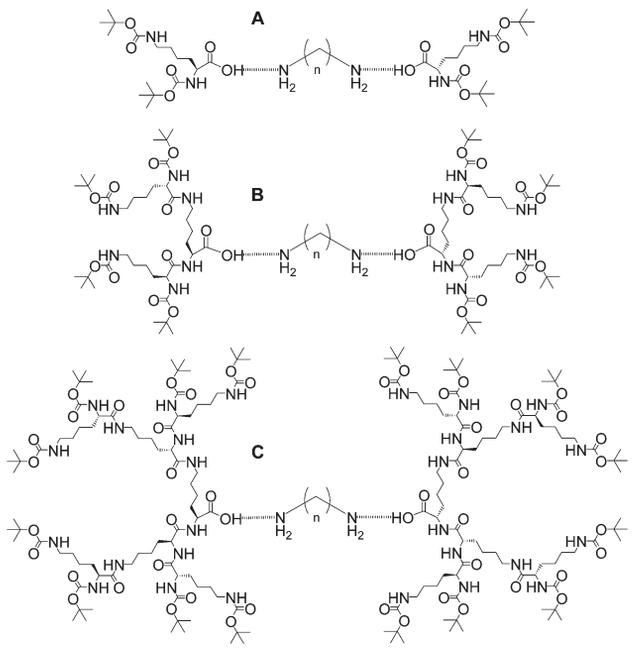

Fig. 1 Structure of the two-component gelators investigated in this paper. A = **G1··C12··G1**, B = **G2··C12··G2** and C = **G3··C12··G3**.

assembly, and hence determines the extent of fibre formation and thus the macroscopic gelation.

In this paper, we investigate the effect of dendritic generation on the assembly process. We find that, for this two-component system, there is an optimum gelator building block, which is the second generation dendron. The first and third generation dendrons are significantly less effective. We relate these observations to a qualitative thermodynamic framework, which outlines the key parameters that should control the assembly of gel-phase materials.

In qualitative terms, we propose that the self-assembly process for gel-phase materials can be related to the following factors:

(i) A favourable enthalpic contribution, due to the formation of favourable intermolecular interactions (*e.g.* hydrogen bonds) between adjacent gelator units within the gel-phase assembly (and for a two-component gel, between the individual components in the gelator complex),

(ii) An unfavourable enthalpic packing term that reflects steric hindrance experienced as a consequence of self-assembly,

(iii) An unfavourable entropic term relating to the assembly of the gelator complex into a specific one-dimensional assembled superstructure (and in the case of a two-component gel, for the formation of the rudimentary gelator complex from its two individual components).

Clearly, this view is somewhat simplistic as it neglects solvent effects, which will also play a significant role in the gelation process.[12] However, for the studies in this paper, each dendritic system is investigated under the same solvent conditions, and hence the thermodynamic role of the solvent is not explicitly considered. The balance of thermodynamic factors outlined above is useful for contemplating the results reported in this paper and the possible origins of any dendritic effects.

Results and discussion

Synthesis

The L-lysine based dendritic branches[13] (dendrons) were synthesised divergently, in optically pure form, and in high yields, using a divergent solution phase approach based on that previously reported,[14] with column chromatography being employed to isolate the purified material. First (**G1**), second (**G2**) and third (**G3**) generation dendritic branches were investigated in this study. Using these dendrons we investigated three different two-component gelator systems: **G1··C12··G1**, **G2··C12··G2** and **G3··C12··G3** (Fig. 1).

Thermal behaviour of the gel-phase materials

In order to assess the structuring behaviour of the different gelator units, the transition from an immobile to a mobile self-assembled state was determined using tube-inversion experiments.[15] All the gel-phase materials reported here were generated using a 2 : 1 dendritic branch : diaminododecane ratio and were thermo-reversible and optically clear, indicating good solubility of the two-component system under all conditions. As previously reported, the effect of molar concentration on the T_{gel} may be described in terms of two distinct regions.[11] Increasing the molar concentration of the gelator unit increases T_{gel} until a 'concentrated regime' (plateau region) is reached, characterised by a concentration-independent T_{gel} (Fig. 2). In this concentration range, we propose that the formation of the gel-phase network is essentially complete.[16]

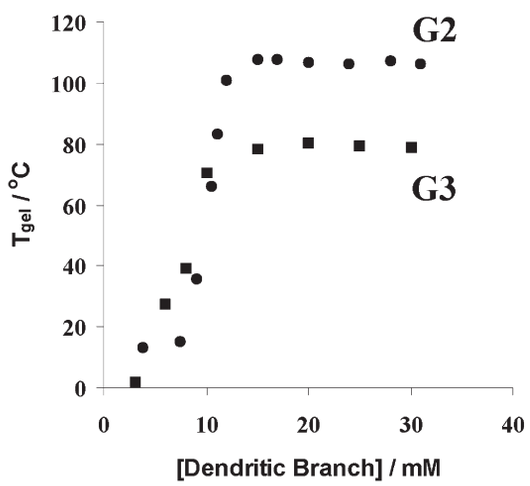

Fig. 2 Effect of the concentration of second (**G2**) and third (**G3**) generation dendritic branches on the gel–sol transition temperature (T_{gel}) in toluene.

It was found that the dendritic branch plays a crucial role in modulating the thermal properties of the gel. Complex **G1··C12··G1** was unable to gelate toluene even at a dendron concentration of 100 mM. However, the solution formed was optically transparent, indicating that solubilisation of the basic diamine spacer unit by the acidic dendritic peptide and formation of a two-component complex had nonetheless taken place. Both **G2··C12··G2** and **G3··C12··G3** two-component systems induced macroscopic gelation. A significant difference between the two dendrons in terms of thermal stability was observed. The T_{gel} plateau values were dependent on the extent of dendritic branching present. Hence, **G2··C12··G2** has a T_{gel} of 104 °C, whilst **G3··C12··G3** has a T_{gel} of 80 °C. Therefore, whilst some branching appears to be essential for gelation, excessive dendritic functionalisation appears to have a negative effect on the thermal stability of the gel.

The thermal behaviour of the second and third generation gel-phase materials was also characterised using differential scanning calorimetry (DSC). The DSC traces were obtained using chlorobenzene as the solvent. Chlorobenzene replaced toluene as the solvent of choice as it exhibits similar physical properties to toluene but importantly has an elevated boiling point, which allowed the DSC measurements of **G2··C12··G2** to be performed, without interference from solvent evaporation.

As shown in Figs. 3A and B, the DSC traces were dependent on the level of dendritic branching. Gelator **G2··C12··G2** (Fig. 3A) exhibited a fairly broad endothermic trace (20–100 °C) indicative of an incremental decrease in the degree of order as a function of temperature. Interestingly, the T_{gel} values obtained using the tube inversion method were comparable to the sharp endothermic peak observed at 100 °C. It seems likely that the T_{gel} values determined by the tube inversion method relate to the temperature at which the number of 'linkages'

in the immobile gel drops below a critical network density.[17] Conversely, **G3··C12··G3** (Fig. 3B) exhibited an extremely broad endothermic trace with a small maximum at ~60 °C and a larger peak beginning at ~80 °C. This increased broadness of the DSC trace typifies a less cooperative transition from an immobile gel to an isotropic state. This indicates that the gel constructed from **G3··C12··G3** is much less ordered than the gel based on **G2··C12··G2**. No DSC trace could be obtained for **G1··C12··G1** as the degree of macroscopic ordering is negligible.

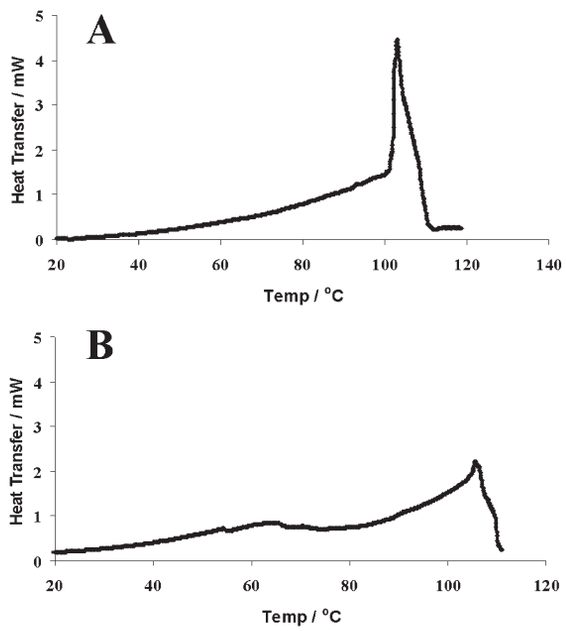

Fig. 3 Differential scanning calorimetry endotherms in chlorobenzene. [Dendritic branch] = 20 mM. A: **G2··C12··G2**, B: **G3··C12··G3**.

Morphological properties of the self-assembled materials

Molecular self-assembly at the nanoscale level can be observed using scanning electron microscopy (SEM). This technique provides a comparative visual technique to assess the impact of the size of the dendritic peptide on the mode of self-assembly. Figs. 4A–C show a series of SEM images of **G1··C12··G1**, **G2··C12··G2** and **G3··C12··G3**. The same concentration of gelator unit was employed in each case.

SEM revealed that the morphology of the self-assembled state is directly controlled by the 'size' of the dendron. **G1··C12··G1** formed 'sausage-like' morphologies, rather than fibres. It should be noted that the diameter of these morphologies is ~100 nm—much wider than a single gelator unit. This indicates that **G1··C12··G1** does not possess the required 'level' of directional organizational 'power' to form a fibrous nanoscale architecture, even though some self-assembly is visualised using SEM.

Organogels assembled from **G2··C12··G2**, however, formed thin fibres that underwent further aggregation to form bundles of fibres. These bundles of fibres constitute a highly developed entangled network. The high aspect ratio of the individual fibres is indicative of uni-directional 'stacking' of gelator units. Analysis of the individual fibres showed that they are approximately 15 nm wide and several hundreds of nanometres long.

For the **G3··C12··G3** organogel, thick bundles of less well-defined fibres were prevalent, forming a 'loosely woven' network. This is consistent with the lower thermal stability of these gels in comparison to **G2··C12··G2**, and indicates that increasing the size of dendrons to **G3** probably disrupts the anisotropic orientation of the hydrogen bonding amide groups between adjacent dendritic head groups—*i.e.*, the process which yields fibres.

Circular dichroism (CD) studies

It is well-known that circular dichroism (CD) spectra appear when chromophoric moieties are organised into an appropriate chiral or helical orientation.[18] The inherent chirality present in the dendritic peptides and the specific orientation of the amide carbonyl groups allowed the three-dimensional structure of the aggregated state to be studied in this case. The investigation was performed in the dilute state (*i.e.*, at concentrations below the threshold required for macroscopic gelation—which is *ca.* 10 mM) using cyclohexane as the aprotic solvent. Cyclohexane replaced toluene as the solvent of choice as it exhibits similar physical properties to toluene but importantly is UV 'silent' across the wavelength region of interest (*i.e.*, ~220 nm).

Fig. 5A reveals that the **G1··C12··G1** self-assembled state is CD 'silent', indicative that no supramolecular chiral organisation occurs. This indicates that even though the basic diaminododecane was solubilised by the acidic dendritic peptides, the complex does not self-assemble into a structure with chiral, or helical, organisation. This agrees with the observation of 'sausage-like' morphologies by SEM.

CD bands were observed for the assemblies formed by **G2** and **G3**, with λ_{max} values at *ca.* 222 nm, ascribable to the amide carbonyl group of the dendritic peptides. This suggests that in the case of **G2··C12··G2** and **G3··C12··G3** a 'stacked' or helical arrangement is present in the self-assembled state, even below the gelation threshold. Unfortunately, exciton coupling bands that are useful for prediction of the directionality of helicity were not observed. In each case, the CD band has the same negative sign, and this indicates that the bias of the organised supramolecular chirality (or helix) has the same directionality in each of the gel assemblies. Interestingly, the degree of helicity was maximised when the self-assembled state was composed of **G2··C12··G2** gelator units. It may have been expected that increasing dendritic generation from **G2** to **G3** would increase the CD signal, as a consequence of the increased number of CD-active amide groups. It was therefore particularly interesting to note that the CD signal for the **G3··C12··G3** assembly was less intense. This suggests that the **G2··C12··G2** self-assembled state really does form an optimum assembly, with a high degree of chiral organisation, and that switching the 'size' of the dendrons from **G2** to **G3** significantly disrupts the helical stacking. This is consistent with previous studies, which have indicated that the ellipticity is linked to the alignment and binding strength of intermolecular hydrogen bonding between dendritic peptide units.[11d]

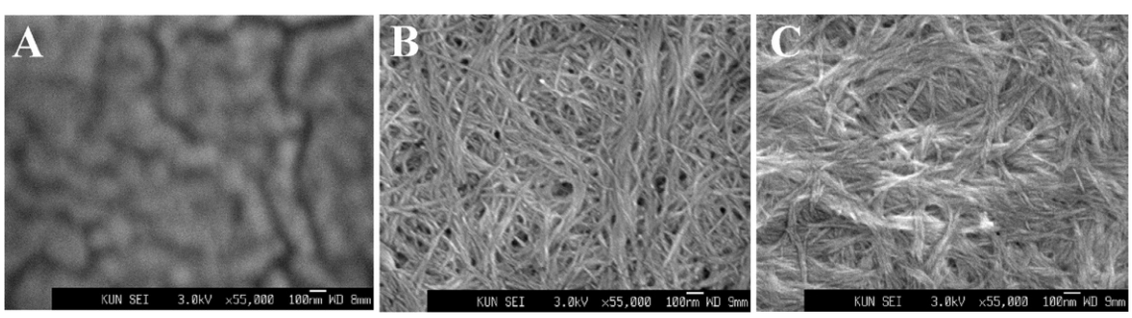

Fig. 4 Effect of dendritic branching on aggregate morphology determined using SEM, [Dendritic branch] = 5 mM and [C12] = 2.5 mM. A: **G1**, B: **G2**, C: **G3**.

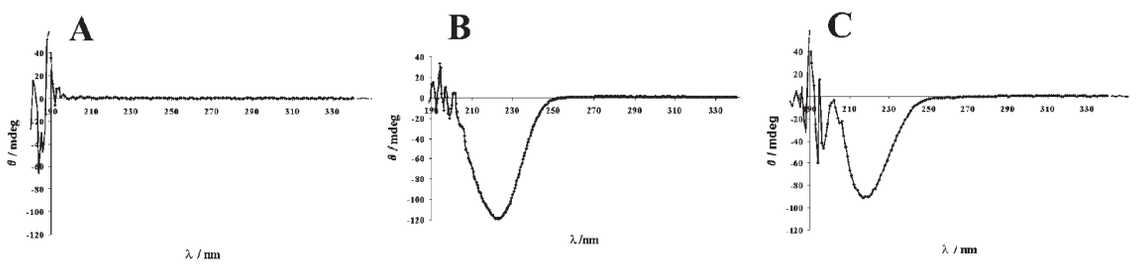

Fig. 5 CD spectra of self-assembled materials (below the gelation threshold concentration) in cyclohexane at room temperature, [dendritic peptide] = 3 mM, [C12] = 1.5 mM, A: **G1**, B: **G2**, C: **G3**.

^{1}H NMR measurements

In general, NMR techniques can provide a large amount of information relating to the self-assembly of the gel-state.[19] The ^{1}H NMR spectra of the **G1** dendron both alone and in the presence of the C12 spacer unit were recorded in d_8-toluene at room temperature. When the C12 spacer was added to the dendron solution, there was a marked downfield shift in the two carbamate (N–H) proton resonances (from *ca.* 5.4 and 4.5 ppm to *ca.* 6.0 and 4.9 ppm respectively). This indicates the formation of intermolecular hydrogen bonds on addition of the spacer. This implies, that even though macroscopic gelation is not observed, addition of the C12 spacer induces some order in the solution state.

The effect of changing the temperature on the NMR spectra of **G1··C12··G1** was determined, and the temperature-dependent chemical shifts of the NH protons are shown in Fig. 6A. Temperature-induced upfield shifts were observed, indicating that hydrogen bond interactions involving these protons are broken on raising the temperature. Furthermore, increasing the molar concentration of **G1··C12··G1** at constant temperature resulted in a very weak concentration-induced downfield shift of the NH protons (Fig. 6B). This trend is indicative of a self-assembly process driven by intermolecular hydrogen bonding. However, the small magnitude of the concentration-induced downfield shift suggests that the number and strength of intermolecular peptide–peptide hydrogen bonds is low.

NMR methods were then used to investigate the assemblies based on **G2** and **G3** dendritic peptides. For **G2··C12··G2** at room temperature, the resonance signals of the gelator unit became weak to the point of non-observability. This result implies that the motion of the **G2** head group is severely restricted in the self-assembled state. Fig. 7 illustrates that at 50–70 °C the resonance signals of the amide (N–H) protons of the dendritic head group cannot be observed. Only on heating to 80 °C does the rigidified gel-phase assembly become sufficiently mobile for a peak corresponding to an N–H proton to become visible.

For **G3··C12··G3**, however, broadened resonance signals could still be observed across the whole temperature range. This is indicative of a self-assembled state that retains some mobility and hence long range disorder. This observation correlates with the DSC trace discussed above. When the temperature was increased, the gelator signals of the **G3··C12··G3** (Fig. 8) became stronger, and upfield shifts were observed between 50–90 °C, indicative once again of the breaking of hydrogen bonds within the gel network. In this case, the T_{gel} was determined to be 80 °C by tube inversion methods and the NMR peaks reach a maximum in intensity around this temperature.

Discussion of results

In terms of non-aqueous self-assemblies, structural changes are driven by both enthalpic and entropic contributions.[20] As discussed in the Introduction, the self-assembly of two-component gel-phase materials is driven by a favourable enthalpic contribution, which is offset by an undesirable enthalpic packing effect and an entropic cost associated with the ordering of the system. Any differences in the favourable enthalpic contribution

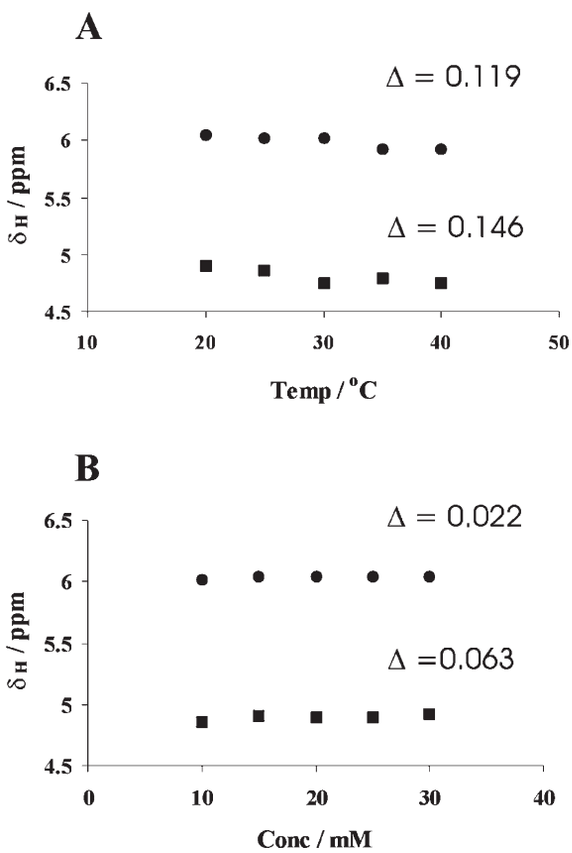

Fig. 6 Effect of temperature (A) and concentration (B) on the resonances of NH carbamate protons in the G1 dendritic branch. A: measured with [dendritic branch] = 20 mM, [C12] = 10 mM; Δ = change in chemical shift on going from 20 to 40 °C. B: measured at 25 °C; Δ = change in chemical shift on increasing dendron concentration from 10 to 30 mM.

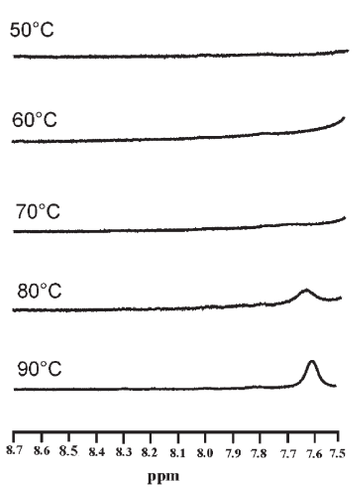

Fig. 7 Effect of temperature on NH resonances of **G2··C12··G2** [dendritic branch] = 20 mM, [C12] = 10 mM.

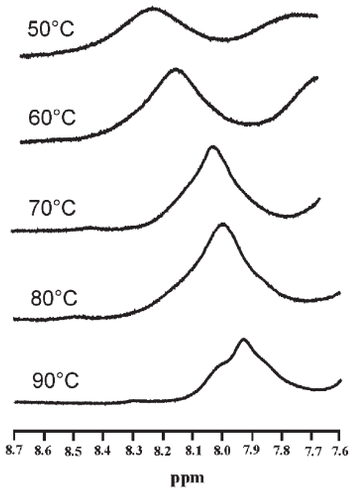

Fig. 8 Effect of temperature on NH resonances of **G3··C12··G3** [dendritic branch] = 20 mM, [C12] = 10 mM.

between **G1**, **G2** and **G3** systems in this case can largely be ascribed to hydrogen bonding (amide–amide interactions between dendritic head groups), particularly given that the spacer unit and the acid–amine interaction which holds the two-components together are both fixed in these investigations. Therefore, the thermal dependence of these gel-phase materials, which is directly linked to the degree of structuring present, is controlled by the effect of dendritic branching on the intermolecular amide–amide hydrogen bonding.

A profound increase in T_{gel} was observed between **G1··C12··G1** and **G2··C12··G2.** This may be attributed to the increased favourable enthalpic contribution due to the greater number of intermolecular hydrogen bonding sites. In simple terms, the benefit of increasing the level of dendritic branching from **G1··C12··G1** to **G2··C12··G2** (*i.e.*, increasing the number of hydrogen bonds) more than compensates for any unfavourable enthalpic packing penalty and any loss of entropy due to hierarchical self-assembly. However, a negative dendritic effect was observed when the peptide 'head group' was increased from **G2** to **G3**, even though there is a formal increase in the potential number of hydrogen bonding sites. The increased 'size' of the **G3** dendron also confers an increased steric (enthalpic) packing penalty on the driving force to self-assembly, in addition to a greater entropic cost of immobilisation. These unfavourable thermodynamic terms for **G3** can clearly offset any increase in the number of hydrogen bonding sites (some of which may also be 'wasted' in intramolecular contacts). This manifests itself macroscopically as a less thermally stable gel.

Unfortunately, due to the broad endothermic traces observed, it was impossible to use DSC to derive meaningful $\Delta H_{gel-sol}$ values using thermodynamic models for these gel-phase materials.[21] Furthermore, although it is, in principle, possible to determine $\Delta H_{gel-sol}$ values from phase diagrams,[22] we have found this method gives unreliable results for this two-component system, that are in considerable qualitative disagreement with the endotherms observed by DSC.

The self-assembly of dendritic gelator units can be considered to be similar to that of surfactant molecules. Our observations are, as such, somewhat analogous to Israelachvili's well-established theories dealing with the self-assembly of surfactant molecules into micellar-type aggregates, in which the volume of the polar head group is able to directly control the observed morphology of the self-assembled superstructure.[23] This theory has been previously applied to understanding the effect of dendritic generation on the self-assembly of dendritic surfactants into different morphologies.[24] It is our argument that in these gel-phase materials, the extent of dendritic branching modulates the spatial orientation and binding energy of the amide–amide hydrogen bonds responsible for fibre formation.

Comparing dendritic effects on gelation

As discussed in the Introduction, we recently published the dendritic effects of a one-component gelator system based on a similar structure, but with L-lysine dendrons covalently linked to a core disulfide moiety.[10] It was found that in this case, higher generation dendrimers gave rise to more thermally stable gels (**G3** > **G2** > **G1**). Meanwhile, Kim and co-workers have reported a system which exhibits a negative dendritic effect (**G1** > **G2**).[9] In this paper, however, we report that there is an optimum level of branching for gel-phase materials behaviour. Clearly, despite the significant differences in reported dendritic effects, the thermodynamic factors which control the assembly of gel-phase materials should be similar in each case, as outlined in the Introduction. We therefore propose that the balance between favourable and unfavourable thermodynamic factors probably determines the nature of the dendritic effect. For a *positive* dendritic effect, the extra branching must provide favourable enthalpic interactions which outweigh the unfavourable steric interactions and entropic cost of immobilisation. For a *negative* dendritic effect, the unfavourable steric interactions and entropic cost of immobilisation must outweigh any additional favourable enthalpic interactions. For an *optimum* dendritic effect, these factors must be in a subtle balance, with a degree of branching being favoured due to the additional favourable enthalpic interactions, but too much branching being disfavoured because of the steric and entropic cost of the aggregation process.

Although the nature of the thermodynamic factors should be similar for all gelation processes, there is also a fundamental difference between one-component and two-component gelation systems[25]—for one-component gelators, there is no need for the rudimentary gelator complex to form from its two individual components—a process which has a favourable enthalpic contribution but an unfavourable entropic cost. In order to develop an enhanced understanding of these differences, we are currently investigating the direct covalent analogues of the two-component gelators reported in this paper (with a diaminododecane spacer chain covalently connected between two dendritic L-lysine head groups). The results of this study will be reported in due course.

Conclusions

Diaminododecane was solubilised by L-lysine based dendritic peptides, and these two component gelator units self-organise to form supramolecular assemblies in aprotic organic solvents (*e.g.* toluene, chlorobenzene and cyclohexane). The propensity for, and mode of, self-assembly are modulated by the size of the dendritic peptide (*i.e.*, the generation of dendritic branching). Intriguingly, the maximum thermal strength materials (reflected by T_{gel} values) were attained when the second generation dendron was used. NMR and CD investigations indicated the importance of hydrogen bond interactions and the greater propensity of the second generation dendrons to form a chirally organised assembly. We therefore argue that the *optimum* second generation building block for this gelation system reflects an ideal balance between a favourable enthalpic contribution (*i.e.*, amide–amide hydrogen bonding) and unfavourable steric enthalpic and entropic terms. We also believe this balance between thermodynamic factors can explain the variety of different dendritic effects reported for gel-phase materials. Preliminary results indicate that this two-component system behaves in a different way to a similar one-component system, and further research will attempt to elucidate the differences between one- and two-component gelators in a more precise manner.

Experimental

Materials

All dendritic branches were synthesised as reported previously,[14] using a divergent approach. Diaminododecane was used as supplied by Aldrich.

Gelation experiments

The experiment was performed by solubilisation of a weighed amount of dendritic gelator in a measured volume of selected pure solvent. The mixture was sonicated at ambient temperature for 30 min before heating and cooling produced a gel. The gel sample was left to stand overnight. Gelation was considered to have occurred when a homogenous 'solid-like' material was obtained that exhibited no gravitational flow. The thermally reversible gel–sol transition temperature (T_{gel}) was determined using a tube inversion methodology.

Differential scanning calorimetry

The thermograms were recorded on a SEIKO DSC 6200 instrument using closed stainless steel cups. The gelator was placed in the stainless steel cups and the run was recorded (in triplicate). The scan speed for the heating cycle was 5 °C min^{-1}. Calibration was preformed using a sapphire standard.

Scanning electron microscopy

Gel samples were applied to stainless steel stubs and allowed to dry. Prior to examination the gels were coated with a thin layer of gold/Pt (60 : 40). Scanning electron micrographs were recorded using a Jeol JSM-6330F instrument. Au/Pt deposition was performed using a Denton vacuum LLC.

Circular dichroism measurements

Circular dichroism (CD) spectra were recorded (200–350 nm) using a JASCO 810 spectrometer and a 1.0 mm quartz cuvette. A sample interval of 1 nm and an averaging time of 3 s were used in all experiments. [Dendritic branch] = 3 mM.

VT ^{1}H NMR measurements

^{1}H NMR spectra were recorded on a JEOL 400 spectrometer. Chemical shifts are denoted in δ units (ppm) relative to toluene (^{1}H: δ = 7.16 ppm and 2.1 ppm) and chlorobenzene (^{1}H: δ = 7.3 ppm). All experiments were carried out with the following parameters: scan rate = 1000, relaxation time = 2 s.

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