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PAPER

Amino acid based low-molecular-weight tris(bis-amido) organogelators†

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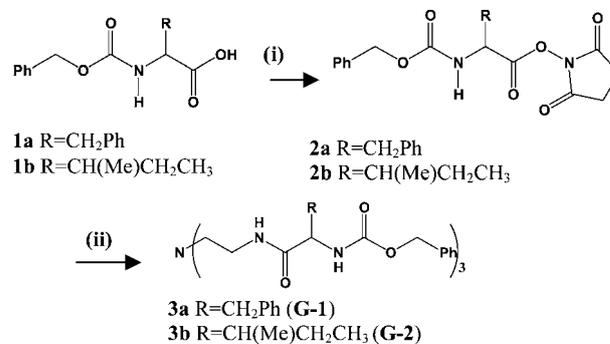
Two new amino acid based low-molecular-mass organic gelators were designed, synthesized, and examined for their ability to gelate various organic solvents. The gelator molecules were found to aggregate *via* N–H⋯O hydrogen bonding to form an interwinding 3D network which immobilized a large number of organic solvents. Among the different organic solvents used in the gelation study mesitylene is found to be the best solvent. The microstructure of organogels was studied with FESEM and optical micrographs. The involvement of hydrogen bonding in the aggregation of the gelator molecule was studied using temperature dependent ¹H NMR. The obtained organogels were found to exhibit significant mechanical strength.

Introduction

Gels have potential applications in drug delivery, cosmetics, cleaning agents, sensors, polymers, tissue engineering, enzyme-immobilization matrices, as well as in phase selective gelation and water purification by dye absorption.^{1,2} A very wide variety of low-molecular-mass organic gelators (LMOGs) are known in the literature.^{3,4} The common forces which are responsible for supramolecular gel formations are some specific or noncovalent interactions, such as electrostatic, dipole–dipole, hydrogen bonding (H-bonding), π – π stacking, and van der Waals interactions. The new molecular gelators with predefined properties can be designed by the proper understanding of molecular geometry as well as the various intermolecular forces. About two decades ago Weiss and Lin serendipitously discovered the gelling ability of a steroid derivative.⁵ Currently several different approaches exist in the literature depending on the nature of gelators. Several versatile molecules were shown to act as gelators *viz.* fatty acid derivatives, steroid derivatives, anthryl derivatives, molecules containing steroidal and condensed aromatic rings, dendrimers *n*-alkanes, oligo(*p*-phenylenevinylene), dipyriddyurea–carboxylic acid combination, diamine linked dendron, *etc.*⁶ To design a new gelator molecule the understanding of molecular geometry as well as the various intermolecular forces is an essential requirement. These inputs can be readily availed from the wealth of information that exists in the solid-state chemistry.⁷ For example, recently, in several cases, the structure of gels was established by studying and understanding the crystal structures of gelator molecules. In one of the recent examples reported by Steed *et al.*, it has been shown

that a chiral tripodal urea is an excellent LMOG to form elegant helical gel fibers from aqueous methanol or from aqueous DMSO solvent.⁸ The helicity of the fibers was explained on the basis of their intermolecular aggregation in the crystal structure. Further, several groups have reported that the amino acid containing straight chain amide molecules can also act as gelators.^{2b,2d,9}

The use of amino acid containing compounds as gelators (LMOGs) is very important due to their inherent biocompatibility and easy functionalization for tuning the properties. These qualities make LMOGs containing amino acids as excellent candidates for the application in biomedical area.¹⁰ In the present paper we would like to explore the self-assembly behavior of a new tripodal chiral ligand (Scheme 1), linked with amino acid units, particularly in their gel state and deduce the structure and properties by various spectroscopic and other studies. The molecules **3a** (G-1) and **3b** (G-2) were chosen for our studies due to the following reasons. The presence of six amide moieties can drive the aggregate formation through amide-to-amide N–H⋯O hydrogen bonding. The nature of the



Scheme 1 Synthetic route to compounds G-1 and G-2. (i) *N*-Hydroxy succinimide; DCC, dry THF, 0 °C, 5 h; (ii) (a) tris(2-aminoethyl)amine, DME, 0 °C, 18 h; (b) reflux, 60 °C, 6 h.

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aggregation is predictable to some extent as there exists enormous literature on the amide recognition patterns, especially for the long alkyl substituents, bis- and tris(urea) LMOG derivatives, which have proved to be highly effective gelators.¹¹ The hydrophobic attachments on the arms of the molecule can be varied according to the requirements of the organic solvents. The presence of L-amino acid moiety relates to the biologically important peptide derivatives. Another interesting feature of these molecules is the chirality, which is expected to transfer into the supramolecular aggregation.

Result and discussion

Gelation behavior

Our initial efforts to crystallize these tripodal compounds **G-1** and **G-2** for establishing their aggregation in the solid state were unsuccessful, despite several trials in different solvents and conditions. Interestingly, on the other hand, we have found a series of solvents in which the molecules **G-1** and **G-2** form transparent, stiff and thermo-reversible gels (Fig. 1). The gel formation in different solvents is confirmed by 'inverted vial' method (Fig. 2). The gelation behavior of **G-1** and **G-2** has been summarized in Table 1. These two gelator molecules exhibit gel formation ability with a large number of organic solvents. The organogels were found to be stable at room temperature for six to eight months. In all the cases, the gels show thermoreversibility since the aggregation occurs through the weak interactions. To compare gelation abilities, MGC (Minimum Gelator Concentration) values (Table 1), which is defined as the minimum amount of gelator required to gelate a given volume of solvent, have been determined for both gelators **G-1** and **G-2**. The aromatic solvents containing alkyl or halogen group attached to it were found to be preferably trapped by the gelator **G-1** or **G-2**. This could be due to increased self-aggregation of **G-1** or **G-2** due to the hydrophobic nature of aromatic solvents towards the hydrophilic functional groups, such as amides. Further, this analogy was supported by the gelation studies with solvents containing hydroxyl groups which have not resulted in the gel formation in spite of good solubility of the gelators in those solvents. This proves that the aggregation of the gelator molecules was not possible if solvents contain functional groups capable of forming hydrogen bonds with gelators.

Some important conclusions can be drawn from the results summarized in Table 1. The increase of the number of

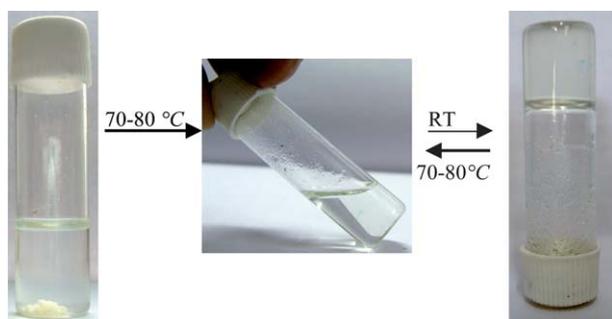


Fig. 1 Illustrations depicting the thermoreversibility of the gelators (in mesitylene) by inverted vial method.



Fig. 2 Gels formed by **G-1**: (1) *o*-xylene; (2) toluene; (3) benzonitrile; (4) chlorobenzene; (5) bromobenzene; (6) iodobenzene; (7) *m*-xylene; (8) ethyl benzene; (9) *p*-xylene; (10) nitrobenzene and (11) benzyl chloride.

substitutions on the aromatic ring of a solvent decreased the MGC values for both **G-1** and **G-2**. In other words, **G-1** or **G-2** is a good gelator for mesitylene than xylenes or toluene. The studies with *o*-xylene and *p*-xylene indicate the position of methyl does not have significant effect on MGC. However, a marginal increase in MGC value was observed when the methyl group (toluene) was changed to ethyl group (ethyl benzene). Among all the solvents studied mesitylene is found to be the best gel-forming solvent. This could be due to the match in the symmetries of gelator and mesitylene. In the case of halo-substituted aromatic solvents chlorobenzene is found to be the better gel-forming solvent than bromobenzene or iodobenzene. This result reflects in the better intermolecular interactions (due to polarization) of iodo derivative with the gelator, thereby reducing the gelation capability. Similarly, the reduction of gelation capability was also observed in the case of nitrobenzene or benzonitrile both of which have an excellent capability of hydrogen bonding to amides of **G-1** and **G-2**.

Thermal behaviour

The thermal stability of the organogels was investigated by measuring the gel-sol transition temperature (T_{gel}). It was

Table 1 Gelation properties of **G-1** and **G-2**^a

Solvent used	Gelation behavior		MGC/mg mL ⁻¹ ($T_{gel}(\pm 1\text{ }^\circ\text{C})$)	
	G-1	G-2	G-1	G-2
Methanol	CL	CL	—	—
Ethanol	CL	CL	—	—
Chloroform	CL	CL	—	—
Dichloromethane	CL	CL	—	—
Acetonitrile	CL	CL	—	—
Nitrobenzene	Y ^a	Y ^b	16.1 (80)	—
Benzonitrile	Y ^a	Y	33.3 (64)	25.0 (82)
Benzylchloride	Y ^a	CVL	40.0	—
Chlorobenzene	Y ^a	Y ^a	14.0 (88)	16.0 (85)
Bromobenzene	Y ^a	Y ^a	20.0	20.0 (98)
Iodobenzene	Y	Y	22.2 (73)	21.0 (87)
Toluene	Y	Y	7.6 (78)	7.2 (82)
<i>o</i> -Xylene	Y	Y	7.1 (83)	7.1 (97)
<i>m</i> -Xylene	Y	Y	6.3 (86)	7.1 (90)
<i>p</i> -Xylene	Y	Y	7.7 (86)	7.1 (90)
Ethylbenzene	Y	Y	6.0 (83)	7.0 (91)
Mesitylene	Y	Y	4.6 (98)	5.8 (95)
Acetophenone	—	Y	—	12.5 (80)
Cyclohexanone	CVL	Y ^a	—	15.0
Hexane	INS	INS	—	—

^a INS = insoluble, Y = forming gel within 30 min, Y^a = it takes several hours to form gel, Y^b = gel formed after some days, CVL = clear viscous liquid, CL = clear liquid, '—' = suitable data were not found.

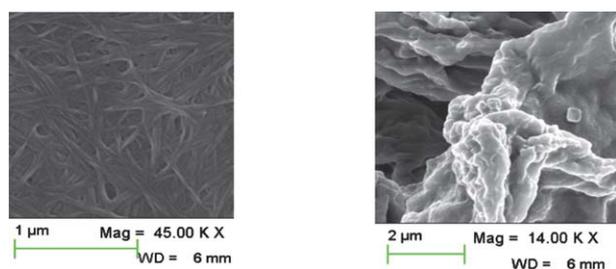


Fig. 3 FESEM images of organogels. Left image—**G-1**, dried gel from mesitylene; and right image—**G-2**, dried gel from mesitylene.

determined by heating the sample vial in the temperature-controlled water bath until tube inversion showed that the gel had melted. The higher thermal stability of the organogels in different solvents is shown by the high T_{gel} values (Table 1) and can be attributed to the stronger H-bonding interaction among gelator molecules. Mesitylene was found to be the best solvent for the gelation which led to the formation of very tightly bound networks through strong intermolecular H-bonding interaction. Consequently, the organogel in mesitylene showed higher thermal stability compared to the organogels obtained from other solvents.

Microstructural study

The microstructure of organogels was examined by a field-emission scanning electron microscope (FESEM). The FESEM image (Fig. 3) of xerogel (dried gel) (**G-1**) from mesitylene shows a 3D network of intertwined ribbons with a width of ~ 100 nm. Such a supramolecular network clearly depicts the better entrapment of the solvent molecule. In the case of dried xerogel **G-2** from the same solvent, a lamellar morphology was observed. This could be due to the presence of different hydrophobic group in the side arm of the gelator molecule.

The visual image of the supramolecular aggregation of organogels **G-1** and **G-2** in mesitylene was also investigated by using a polarised optical microscope (POM). Fig. 4 and 5 show the POM images of the organogels of **G-1** and **G-2**, respectively. That the elongated fibers form a gel network are clearly seen in the POM images.

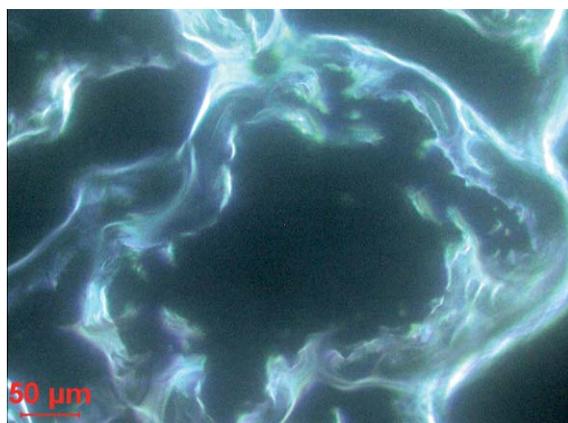


Fig. 4 POM image of **G-1** in 50 \times magnification.

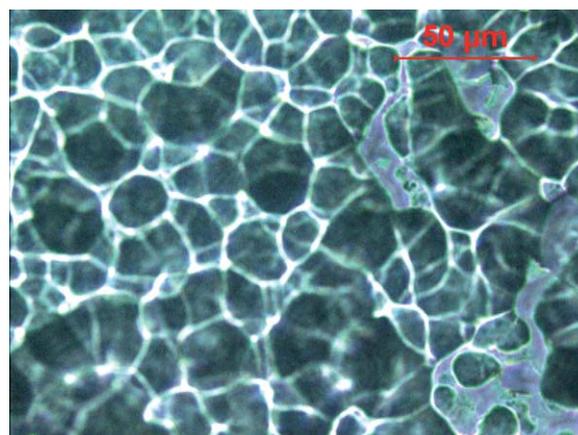
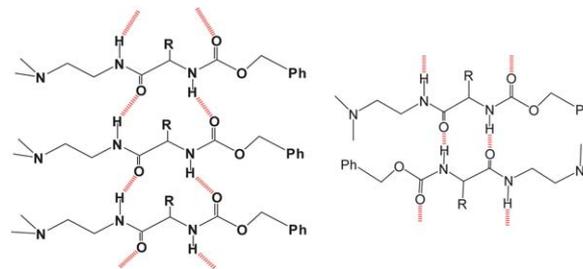


Fig. 5 POM image of **G-2** in 50 \times magnification.

Temperature dependent ^1H NMR study

It is well known that H-bonding is considered to be one of the major driving forces for the supramolecular aggregation of LMOGs.^{1a} Recently a cyclohexane based amide-containing tripodal LMOG has been reported where the molecules stacked through the formation of a triple chain of intermolecular hydrogen bonds.^{12a} From the view point of molecular structure the gelators **G-1** and **G-2** are expected to assemble in a number of ways *via* N–H \cdots O hydrogen bonds. Two of these possible aggregations have been shown in Scheme 2. To get a quantitative idea about the assembly of gelator molecules *via* H-bonding interactions, a systematic temperature-dependent ^1H NMR study was performed by using the saturated solution of **G-1** and **G-2** in CDCl_3 . ^1H NMR measurements of these compounds indicate that the amide protons are sensitive to changes in temperature. At 20 $^\circ\text{C}$ two amide protons of gelator **G-1** appeared at $\delta = 6.095$ and $\delta = 7.538$ ppm, respectively. With the gradual increase in temperature (in steps of 10 $^\circ\text{C}$) these two protons experienced a notably upfield shifts and at 60 $^\circ\text{C}$ the two amide protons appeared at $\delta = 5.89$ ppm and $\delta = 7.256$ ppm, respectively (Fig. S1, see ESI †). Similarly for gelator **G-2** at 20 $^\circ\text{C}$ two amide protons appeared at $\delta = 6.064$ ppm and $\delta = 7.722$ ppm, respectively, which shifted to $\delta = 5.93$ ppm and $\delta = 7.551$ ppm at 60 $^\circ\text{C}$ (Fig. S2, see ESI †). The change in δ value (N–H proton of amino acid part each from **G-1** and **G-2**) with temperature is shown in Fig. 6. These results suggested that in the gel state at room temperature intermolecular N–H \cdots O hydrogen bonding was present between the neighboring amide groups. The observed upfield shift of amide protons with an increase in



Scheme 2 Possible aggregation of gelator molecule *via* N–H \cdots O hydrogen bonds.

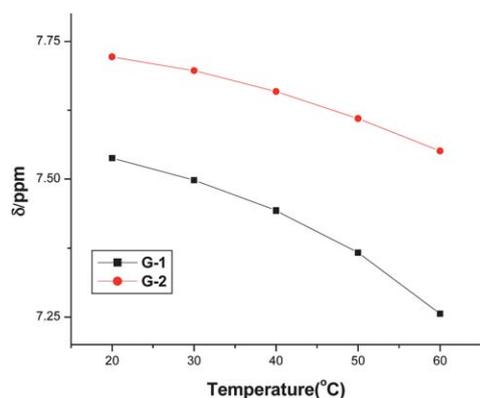


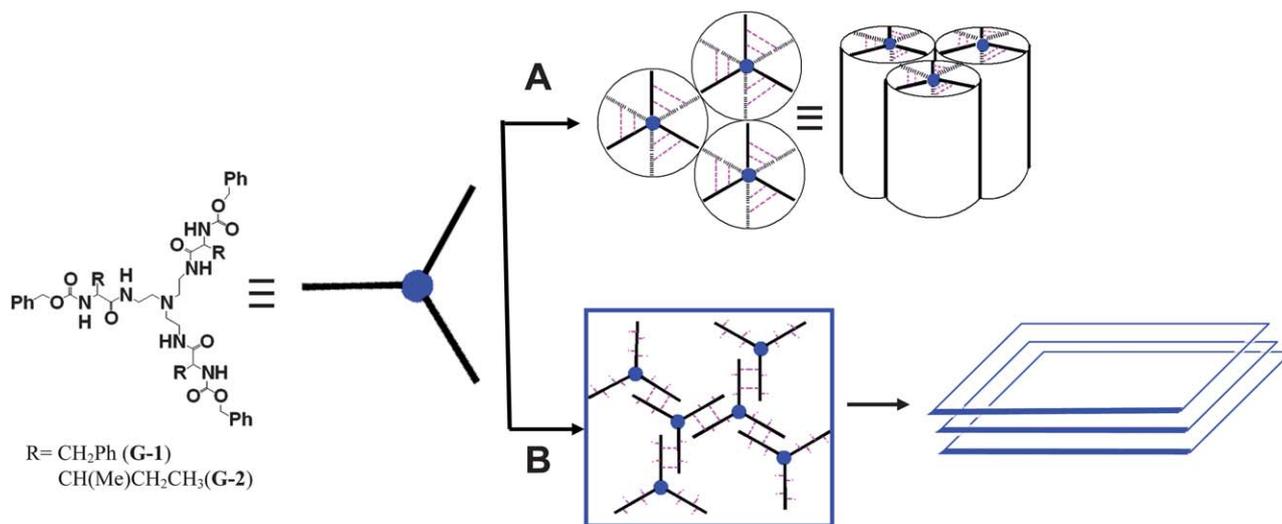
Fig. 6 Temperature-dependent chemical shift of amide protons of **G-1** and **G-2**.

temperature is due to the disruption of intermolecular hydrogen bonds between the amide functionalities leading to the phase transition from gel to sol. From the above experimental evidence it is very much clear that both the amide protons from each arm of the gelator molecules were involved in the formation of N–H···O hydrogen bond which is considered to be one of the most significant driving forces for the supramolecular aggregation of gelator molecule that immobilized the large volume of solvents.

Extensive research works have demonstrated the self-assembling nature of the amide-containing C_3 symmetrical molecules via N–H···O hydrogen bond, particularly in their gel state and solid state.^{8,12} Based on the plethora of existing literature and on our own studies^{7,12d} of the related molecules in the solid state, we would like to propose the columnar or lamellar aggregation of the gelator molecules as the possible models (Scheme 3) for the gelator structures of **G-1** and **G-2**.

Rheology

The rheological behavior is an important factor for the potential applications of the gels. It is strongly influenced by the



Scheme 3 Schematic model for the possible way of aggregation of gelator molecules to form the gel network. (A) Columnar packing and (B) layered arrangement of the gelator molecule.

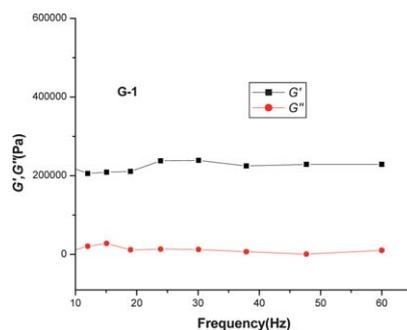


Fig. 7 Variation of storage modulus (G') and loss modulus (G'') with frequency of organogel **G-1**.

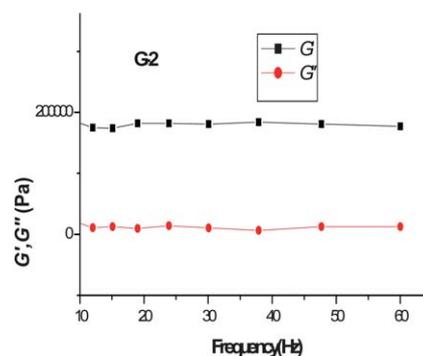


Fig. 8 Variation of storage modulus (G') and loss modulus (G'') with frequency of organogel **G-2**.

supramolecular aggregation of gelator molecules. The rheological analysis provides a detailed information about the structure, consistency and phase transition process. For characterization of the general rheological behavior and to provide information about the stiffness of aggregation we have examined the organogels of **G-1** and **G-2** in mesitylene at room temperature. Frequency sweep rheometry measurement of the organogels (Fig. 7 and 8) indicates that the changes in elastic modulus,

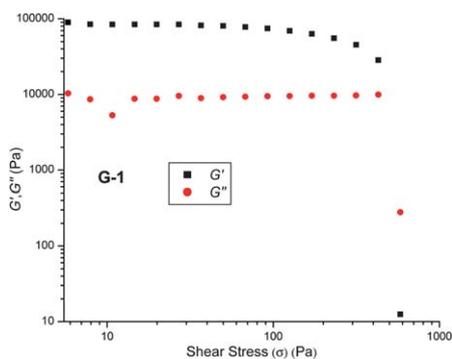


Fig. 9 Variation of storage modulus (G') and loss modulus (G'') with shear stress (σ) of organogel **G-1**.

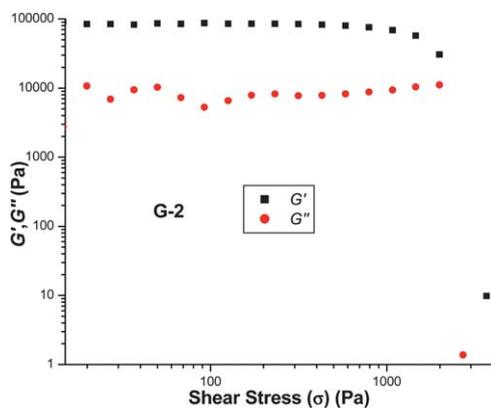


Fig. 10 Variation of storage modulus (G') and loss modulus (G'') with shear stress (σ) of organogel **G-2**.

G' , and viscous modulus, G'' , with frequency follow the same trend, and at any given frequency G' values were much higher than G'' , indicating more elastic nature of the gels like solids. Moreover, both G' and G'' are frequency independent in the linear viscoelastic regime. Such a linear viscoelastic nature is in good agreement with classical gel and supports the belief that these materials undergo a transition to a true gel state. The difference between G' and G'' can be regarded as the indication of rigidity of the gel sample. The ($G' - G''$) values were 2.28×10^5 Pa and 1.77×10^5 Pa for **G-1** and **G-2**, respectively, indicating the firmness and rigidity of the organogels. Fig. 9 and 10 show the plots of G' and G'' against shear stress (σ) at a constant frequency of 1 Hz. It can be observed that above a critical stress value both G' and G'' abruptly fall to a very low value, indicating flow of the organogel. This critical stress value is referred to as yield stress (σ_y). The σ_y value of **G-2** as obtained from the breakpoint of the respective plot is 1481 Pa and that for **G-1** is 316 Pa. The σ_y values are quite large, suggesting high mechanical strength of the organogels. The higher σ_y value of the organogel of **G-2** compared to that of **G-1** suggests its greater mechanical strength.

Conclusions

This study presented a new class of organogelators that form stable gels of significant mechanical strength in aromatic solvents. The solvents such as mesitylene having more electron

rich centre and showing the structural proximity with that of the gelator molecules were proved to be the better solvent for gelation. The gelation process was observed to be thermo-reversible. It is interesting to note here that the urea related gels reported by Steed *et al.* are stable even in the presence of water unlike the present systems.⁸ This could be due to more hydrophobic nature of the **G-1** and **G-2** compared to the urea based gelators. The FESEM image suggests the different nature of aggregation mode that depends on the structure of the gelator molecule. The temperature-dependent ^1H NMR study confirmed the importance of intermolecular H-bonding between amide linkages in the gel-forming process.

Experimental details

Synthesis

N-Hydroxysuccinimide esters of *N*-Cbz-*L*-amino acids (**2a,b**) were synthesized by following a literature procedure.¹³

General procedure for the synthesis of G-1 (3a). The *N*-hydroxysuccinimide ester of *N*-Cbz-*L*-phenylalanine (2.0 g, 5.0 mmol) was dissolved in dry DME (40 mL) cooled in an ice bath. Tris(2-aminoethyl)amine (0.246 g, 1.6 mmol) dissolved in dry DME (15 mL) was added as several small portions to the above solution. The reaction mixture was stirred at room temperature for 18 h and then warmed for 6 h at 40–50 °C. The white solid was filtered off and washed with cold water and cold methanol. Yield (3.80 g, 76%); $[\alpha]_{\text{D}}^{25}$ (1%, CH_3OH) = -1.28 ; mp 167–170 °C; ^1H NMR (200 MHz, CDCl_3) δ 1.26–1.32 (m, 3H), 1.70 (br, 3H), 2.20–2.60 (m, 9H), 2.95–3.07 (m, 6H), 4.78 (d, 3H, $J = 12.6$), 4.91 (d, 3H, $J = 12.6$), 6.04 (br s, 3H), 7.15–7.23 (m, 30H), 7.54 (br s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 33.97, 39.12, 54.91, 56.20, 66.74, 126.68, 127.62, 127.97, 128.36, 128.45, 129.47, 136.37, 136.91, 156.63, 172.39; ESI-MS for $\text{C}_{57}\text{H}_{63}\text{N}_7\text{O}_9$ (**G-1**) $[\text{M}]$, $[\text{M} + \text{H}]^+ = 990.5064$. Anal. Calcd for $\text{C}_{57}\text{H}_{63}\text{N}_7\text{O}_9$: C, 69.16%; H, 6.37%; N, 9.91%; found: C, 68.66%; H, 6.35%; N, 9.93%.

Synthesis of G-2 (3b). This compound was synthesized as described above starting from the *N*-hydroxysuccinimide ester of *N*-Cbz-*L*-isoleucine and tris(2-aminoethyl)amine. Yield (3.18 g, 65%); $[\alpha]_{\text{D}}^{25}$ (1%, CH_3OH) = -4.11 ; mp 192–194 °C; ^1H NMR (200 MHz, CDCl_3) δ 0.853–0.967 (m, 18H), 1.18–1.25 (m, 3H), 1.59–1.79 (m, 6H), 2.37–2.59 (m, 9H), 3.26 (br s, 3H), 4.20–4.28 (m, 3H), 4.91 (d, 3H, $J = 12.4$), 5.02 (d, 3H, $J = 12.4$), 6.03–6.07 (m, 3H), 7.24–7.26 (m, 15H), 7.72 (br s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 10.67, 15.31, 24.97, 37.22, 38.74, 55.12, 59.24, 66.73, 127.60, 127.97, 128.49, 136.58, 157.06, 172.95; ESI-MS for $\text{C}_{48}\text{H}_{69}\text{N}_7\text{O}_9$ (**G-2**) $[\text{M}]$, $[\text{M} + \text{H}]^+ = 888.5341$. Anal. Calcd for $\text{C}_{48}\text{H}_{69}\text{N}_7\text{O}_9$: C, 64.93%; H, 7.78%; N, 11.04%; found: C, 65.66%; H, 7.81%; N, 10.98%.

Methods

The melting point of solid compounds was measured using Fisher Scientific melting point apparatus. Optical rotations were measured with a JASCO (Model P-1020) digital polarimeter. Elemental analysis was carried out in PE 2400 series II CHN analyzer. The ^1H NMR spectra were recorded on an AVANCE

DAX-400 (Bruker, Sweden) 200 MHz NMR spectrometer in CDCl₃ as solvent. All measurements were done at room temperature (298 K) unless otherwise mentioned.

A weighed amount of solid gelators taken in screw capped vials was dissolved in different organic solvents by heating and subsequently allowed to stand at 25 °C in a thermostatted water bath to obtain a stable gel as confirmed by the resistance to flow under gravity upon inversion of the vial.

The gel melting temperature (T_{gel}) was determined by placing the screw capped glass vials containing gels in a temperature-controlled water bath (Julabo, Model F 12) and visually observing the flow upon tilt for every degree rise in temperature.

A Field-Emission Scanning Electron Microscope (FESEM, Zeiss, Supra-40) operating at 5–10 kV was used to get the micrograph. For electron micrographs, the hot sample solution was placed on the aluminium foil, allowed to cool at room temperature and then dried in a desiccator for 24 h. A layer of gold was sputtered on top to make conducting surface and finally the specimen was transferred into the microscope.

For all the gel samples, the rheological measurements were performed on a Bohlin CVO D100 (Malvern, UK) controlled-stress rheometer using a 20 mm diameter parallel plate geometry with a constant tool gap of 200 μm. The organogel was placed on lower plate and a stress amplitude sweep experiment was carried out at a constant frequency of 1 Hz at 25 °C to obtain the storage or elastic modulus, G' , and the loss or viscous modulus, G'' . The frequency sweep measurements were carried out at a constant stress of 300 Pa in the linear viscoelastic range.

The polarizing optical light micrographs for the samples were obtained from a LEICA DMLM (Germany) optical microscope by transmitted light under crossed Nicol and fitted with a JVC-KY-F550E imaging system. The samples for optical microscopy contained gelators at a concentration less than the corresponding minimum gelation concentration. A drop of the liquid was placed on the microscope slide and placed under microscope.

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