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Physical gelation of organic liquids by achiral amino acid based amphiphilic gelators: Effect of chirality

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ABSTRACT

We report gelation behavior of a series of *N*-acyl- β -alanine (C_n - β -Ala) gelators in a variety of organic liquids. The effect of alkyl chain length was studied to elucidate gelation mechanism. The gelation behavior of the C_n - β -Ala gelators was compared with that of corresponding *N*-acyl-*L*-alanine (C_n -*L*-Ala) derivatives. Unlike C_n -*L*-Ala the C_n - β -Ala gelators failed to gel aliphatic hydrocarbons and exhibit phase-selective gelation in the presence of water. The gelation ability of C_n - β -Ala was observed to be poorer than C_n -*L*-Ala gelators. Also C_n - β -Ala organogels are thermally less stable, but they are observed to have higher mechanical strength than C_n -*L*-Ala organogels.

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1. Introduction

The design of low-molecular-weight gelators (LMWGs) that gel organic liquids attracted considerable attention in the past three decades [1–7]. A wide variety of organic molecules with diverse molecular architecture have been accidentally discovered to gel organic liquids at relatively low concentrations. Many of these small organic molecules commonly employed as gelators have at least one stereogenic center. Some reports clearly suggested that the ability to form gels is associated with the presence of stereogenic centers in the gelator molecular structure [1,2]. Although there is no conclusive evidence that only chiral molecules form organogels, the fact that chirality enhances gelling ability has been persistently reported in the literature without any broad explanation. A detailed review on the influence of chirality on gelation was published in 2005 by Huc and coworkers [8]. Smith has also reviewed and discussed the effect of chirality in the self-assembly of nanostructured gel-phase materials [9,10]. It has been known that some amphiphilic molecules containing peptide bonds and chiral centers can gel organic solvents, while racemic compounds or molecules that have no chiral center failed to exhibit gelation [11]. Grahame et al. have investigated the effect of chirality on gelation using 12-hydroxystearic acid (12HSA) [12]. They observed difference in the self-assembly modes between D-12HSA and DL-12HSA. Indeed, chirality is often transferred to the morphology of self-assembled fibers as observed with 12HSA [13]. Bhattacharyya and coworkers have studied gelation behavior of *N*-acyl-*L*-alanine (C_n -*L*-Ala) amphiphiles in aliphatic and aromatic hydrocarbon solvents and in their mixtures [14,15]. The authors noted that the DL-alanine derivative did not produce gel in any

of the solvents employed. Since the corresponding glycine derivative was also found to be a nongelator in these solvents, it was concluded that chirality is essential for gelation by this class of LMWGs. Recently, our group has reported gelation of aromatic hydrocarbon and chlorinated methane solvents by *N*-(4-alkyloxybenzoyl)-*L*-alanine amphiphiles [16]. The corresponding DL-alanine derivative, however, was observed to produce weaker gels as compared to the enantiomerically pure compound. In another publication on the water-induced gelation of organic liquids by *N*-(*n*-alkylcarbamoyl)-*L*-alanine amphiphiles, we have shown that the gelation ability of *N*-(*n*-tetradecyl-carbamoyl)- β -alanine is better than *N*-(*n*-tetradecylcarbamoyl)-*L*-alanine as indicated by the low values of critical gelation concentration (CGC) and higher thermal stability [17]. This led us to believe that perhaps chirality is not mandatory for gelation by this class of molecules. In fact, many achiral LMWGs that gel organic liquids have been reported in recent literature [18–24].

However, the role played by chirality in controlling and mediating the self-assembly of gelators is of particular importance. To further understand the role of stereogenic center in the formation of self-assembled fibrillar networks (SAFiNs), a series of *N*-acyl- β -alanine amphiphiles (C_n - β -Ala) were synthesized and their gelation abilities were tested in a range of organic solvents. The C_n - β -Ala and C_n -*L*-Ala amphiphiles (Figure 1) are structurally similar with the same number of C, H, N, and O atoms, except that the former has no chiral center. Therefore, in order to understand gelation mechanism, the gelation abilities of the C_n - β -Ala amphiphiles were compared with those of corresponding C_n -*L*-Ala amphiphile. The organogels were characterized by a number of techniques, including optical microscopy, field emission scanning electron microscopy (FESEM), rheology, and X-ray diffraction (XRD). The gelation mechanism was investigated using FT-IR and ¹H NMR spectroscopy.

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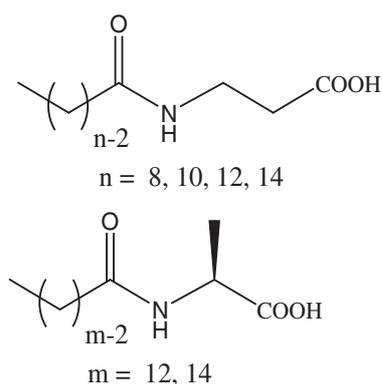


Figure 1. Chemical structures of N-acyl- β -alanine (C_n - β -Ala) and N-acyl-L-alanine (C_n -L-Ala) amphiphiles.

2. Results and discussion

2.1. Gelation behavior of C_n - β -Ala amphiphiles

The gelation test was performed in a series of organic solvents, including aliphatic hydrocarbons, chlorinated methanes, and aromatic hydrocarbons. Gelation behavior of the amphiphiles is summarized in Table 1. As observed, the C_n - β -Ala gelators gel only aromatic solvents. In aliphatic hydrocarbon solvents, the gelators either remained insoluble or precipitated after cooling. In chloroform, the gelators remained soluble. In carbon tetrachloride, however, the gelators exhibit swelling producing partial gel. On the other hand, all the aromatic solvents employed in this work transformed into gel after cooling. In most cases, the organogels appeared optically opaque, but in nitrobenzene solvent, a transparent gel was obtained. This might be due to relatively higher solubility of the gelators in nitrobenzene. The organogels, especially in high-boiling solvents, were observed to be very stable and remained unchanged after a month.

The gelation abilities of the gelators can be compared using CGC values as listed in Table 1. From the data in Table 1 it is clear that CGC values of the gelators lie between 0.5% and 3% (w/v). In a given solvent, the CGC value is observed to decrease with the hydrocarbon chain length of the amphiphilic gelators. Thus lowest CGC value was observed with C_{14} - β -Ala gelator which must be due to the greater van der Waals interaction of the long hydrocarbon chain. It can be observed that for any gelator, CGC value is lowest in mesitylene which is the least polar among the aromatic liquids.

The FESEM images of the xerogels as shown in Figure 2 clearly exhibit three-dimensional (3-D) SAFiNs confirming gelation. All

the images reveal a number of long ribbon-like aggregates, juxtaposed or intertwined by a several long slender aggregates. The 3-D network structure formed by the fiber-like aggregates can also be observed in the optical micrographs (Figure S1, ESI) of the organogels in p -Ph(Me)₂. The XRD patterns (Figure 3) of the gel (in p -Ph(Me)₂) cast films of all the gelators exhibit periodic peaks, suggesting that the gelator molecules are self-assembled into an ordered bilayer structure. The long d -spacing corresponding to 100 plane of the aggregates as obtained from XRD data are 1.60, 2.48, 2.77, 3.12 nm for C_8 - β -Ala, C_{10} - β -Ala, C_{12} - β -Ala, C_{14} - β -Ala, respectively. These values are slightly less than twice the hydrocarbon chain length (1.01, 1.26, 1.51, 1.77 nm, respectively) of the respective gelator molecule. The hydrocarbon chain lengths (the distance between the β -carbon and the $-\text{CH}_3$ group was considered) were obtained from the energy minimized (using MM2 force field of ChemDraw Ultra 7 software) structures of the amphiphiles. This means that the gel aggregates consist of repeating bilayer units in which the hydrocarbon chains are interdigitated in the bilayer self-assembly. This is also indicated by the appearance of a vibrational band at around 1456 cm^{-1} (Figure S2, ESI) due to strong interaction of the hydrocarbon chains [25].

The rheological properties of the organogels of all the amphiphiles were studied at a fixed (0.15 M) concentration in p -Ph(Me)₂ solvent. The organogels formed by C_8 - β -Ala in pure solvents could not resist high mechanical force and break upon shaking of the gel-containing vials. All the other amphiphiles produced sufficiently stronger gels. The organogels of C_n - β -Ala were characterized by stress sweep as well as by frequency sweep rheometry. The frequency sweep measurements (Figure 4) with a small amplitude stress (400 Pa) showed that in every cases, both G' and G'' are almost independent of frequency which is characteristic of gel structure. Also it is observed that at any given frequency, the G' is higher than G'' , suggesting more elastic nature of the organogels, like solids. Figure S3 shows the plots of G' and G'' versus applied 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 values of the C_8 - β -Ala, C_{10} - β -Ala, C_{12} - β -Ala, and C_{14} - β -Ala organogels are 611, 2392, 5375 and 9445 Pa, respectively. The variation of σ_y with the hydrocarbon chain length (C_n) has been shown in Figure 5. It is observed that C_{14} - β -Ala organogel has the highest σ_y value, indicating highest mechanical strength, whereas the C_8 - β -Ala organogel has the lowest σ_y value and hence is the weakest. In fact, the G'/G'' ratio (at 75 Hz), which is a measure of relative elasticity of the organogels, increases in the order C_8 - β -Ala (5.1) < C_{10} - β -Ala (7.5) < C_{12} - β -Ala (9.8) < C_{14} - β -Ala (13.5). This means that the mechanical strength of the organogels increases

Table 1

Gelation abilities of C_n - β -Ala, C_{12} -L-Ala, and C_{14} -L-Ala amphiphiles in different solvents at 298 K. The numbers represent CGC ($\pm 0.1\%$ w/v) values.

Solvent	C_8 - β -Ala	C_{10} - β -Ala	C_{12} - β -Ala	C_{14} - β -Ala	C_{12} -L-Ala	C_{14} -L-Ala
n -C ₆ H ₁₄	I	I	I	I	G	G
n -C ₆ H ₁₂	I	I	I	I	G	G
n -C ₈ H ₁₈	I	I	I	I	G	G
CHCl ₃	S	S	S	S	S	S
CCl ₄	PG	PG	PG	PG	2.0	1.5
PhH	P	2.2	1.5	1.2	1.4	1.2
PhMe	2.6	1.9	1.4	1.2	1.1	0.7
o -Ph(Me) ₂	3.1	2.1	1.6	1.2	1.2	1.0
m -Ph(Me) ₂	2.0	1.2	1.2	1.0	0.9	0.9
p -Ph(Me) ₂	2.6	1.8	1.2	1.1	0.9	0.7
Ph(Me) ₃	1.4	1.3	1.0	0.9	0.8	0.7
PhCl	P	2.3	1.9	1.5	1.5	1.3
PhNO ₂	P	2.0	1.8	1.2	1.5	1.0

S = solution; P = precipitation; I = insoluble, PG = partial gelation; G = gelation.

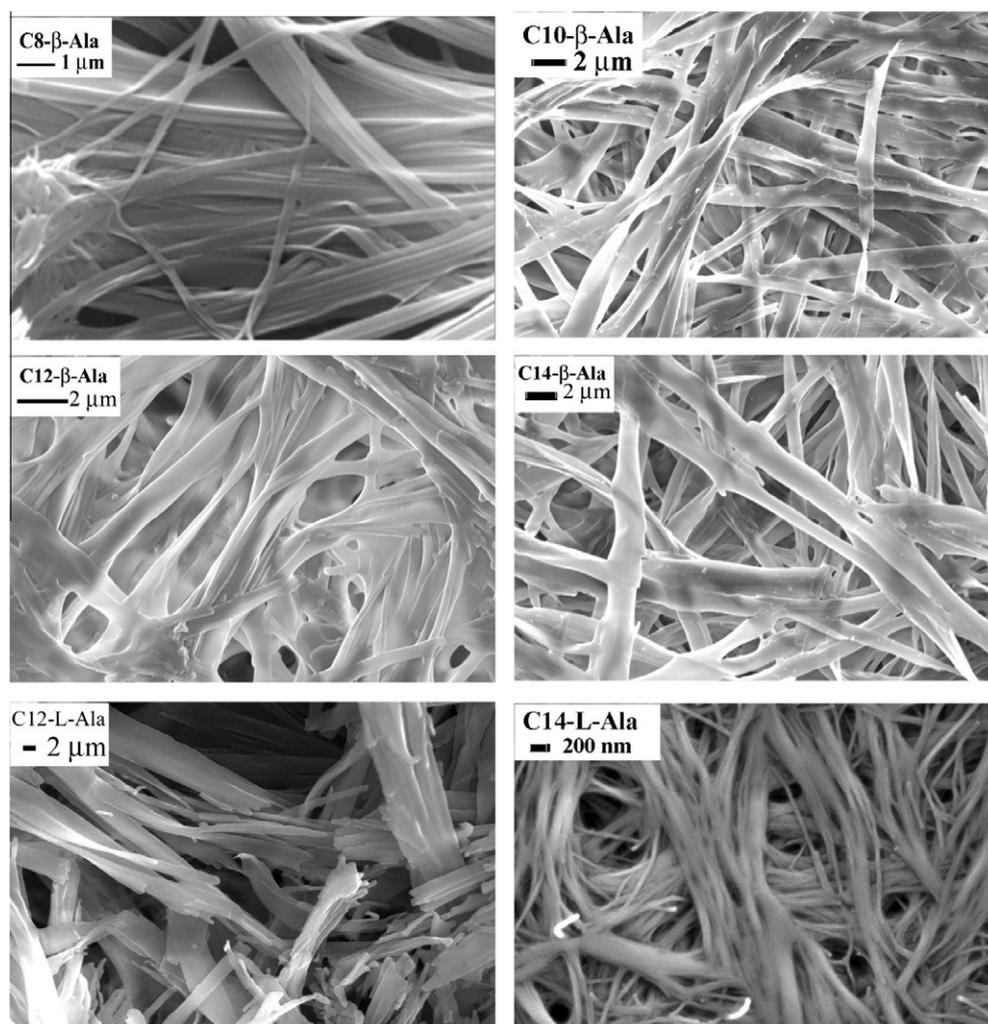


Figure 2. The FESEM images of the air dried organogels containing 0.15 M C_n - β -Ala or C_n -L-Ala in *p*-Ph(Me)₂ solvent at 298 K.

in the order of increasing chain length of the hydrocarbon tail of the amphiphiles. In other words, mechanical strength of the organogels increases with the increase of van der Waals interaction between hydrocarbon tails of the amphiphiles. This shows that the mechanical strength of a gel not only depends on morphology and the degree of non-covalent cross-linking or physical entanglement of the fibrous aggregates forming 3-D network structure, but also on the physical interactions between gelator molecules.

Thermal stability of the organogels was studied by measurement of gel-to-sol transition temperature (T_{gs}). Since T_{gs} value is known to be dependent on the gelator concentration, it was determined at a fixed concentration of 0.05 M for all the gelators in *p*-Ph(Me)₂ solvent. The variation of T_{gs} as a function of C_n of the gelators is shown in Figure 5. It is observed that the T_{gs} value increases with the increase of chain length, indicating increase of thermal stability. This, as suggested by the XRD data, is because of the interdigitation of the hydrocarbon chains in the bilayer aggregate which enhances van der Waals interaction. The results are exactly similar to those reported for C_n -L-Ala amphiphiles [15]. It is interesting to see in Figure 5 that both T_{gs} and σ_y values vary with the increase of hydrocarbon chain length in the same way, which means thermal stability as well as mechanical strength of the organogels depends on the intermolecular forces that drive the gelation process.

2.2. Driving force for gelation

The FT-IR is a useful technique to investigate the driving forces for aggregate formation in solution. Since the morphology of all the gelators is similar, we measured FTIR spectra (Figures S2 and S4 of ESI) of C_{14} - β -Ala as a representative gelator in PhMe and CHCl₃ to consider the factors that are responsible for self-assembly formation. The solvents in which the gelators are soluble it can be assumed that no self-assembly occurs in these solvents. Therefore, the FT-IR spectrum of C_{14} - β -Ala in CHCl₃, which shows the absorption bands at 3440 and 1670 cm⁻¹ characterizes the non-hydrogen-bonded N-H and C=O stretching vibrations of the amide group, respectively. On the other hand, the FTIR spectrum of the organogel in PhMe is almost similar to the spectrum in solid state and is characterized by a band at 3297 and 1632 cm⁻¹ corresponding to N-H and C=O stretching vibration, respectively, of the H-bonded secondary amide group [26]. Also the strongly H-bonded O-H and C=O stretching vibrations of the carboxylic acid group at 3048 and 1690 cm⁻¹, respectively, could be detected in the FTIR spectrum. In support of the results obtained from IR spectral studies, we have also measured ¹H NMR spectra (Figure S5) of C_{14} - β -Ala in concentrated as well as in dilute solution in CCl₄ solvent. It was observed that amide NH(CO) proton absorption peak is broadened and the corresponding chemical shift position moved down field by 0.72 ppm in going from dilute to the

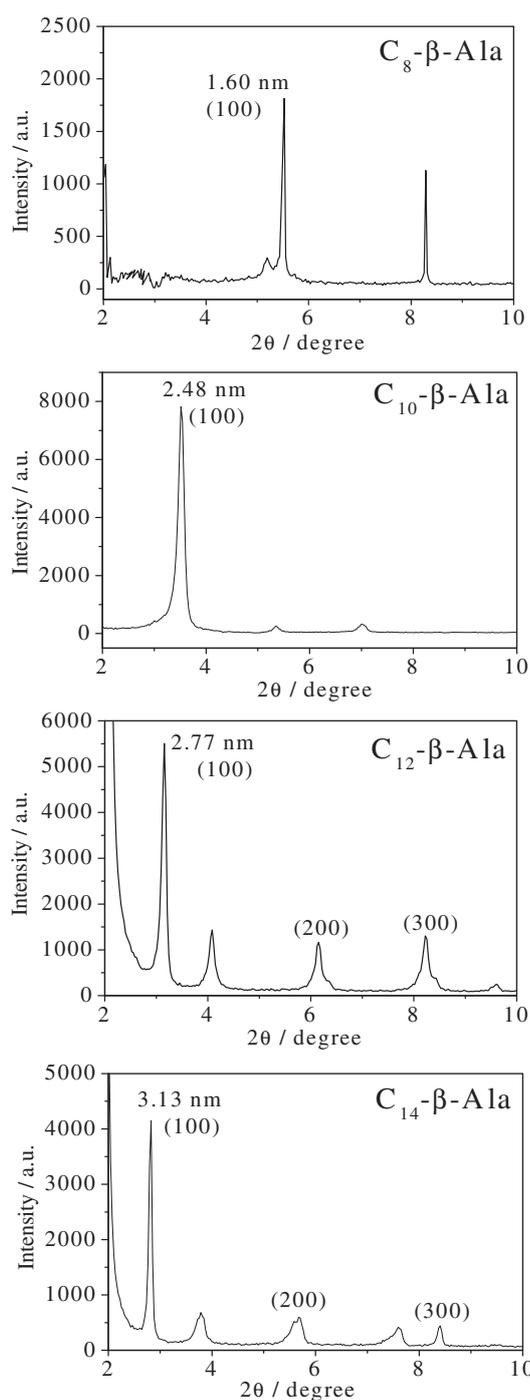


Figure 3. The XRD spectra of the air dried organogels containing 0.15 M C_8 - β -Ala, C_{10} - β -Ala, C_{12} - β -Ala, C_{14} - β -Ala or C_{14} -L-Ala in p -Ph(Me)₂ solvent.

concentrated solution, suggesting intermolecular H-bonding interaction through the secondary amide group of neighboring gelator molecules. Existence of H-bonding interaction is further supported by the fact that the organogels break down when a small volume of tetrabutylammonium fluoride was added to the gel. The F^- ion is known to be a strong H-bond acceptor and thus breaks the amide H-bonding between gelator molecules. This suggests that the driving force for the self-assembly formation is mainly H-bonding which propagate in one dimension forming long fibers. Within the bilayer unit, the amphiphiles are connected with intra- and inter-layer H-bonds. However, it should be noted that self-assembly

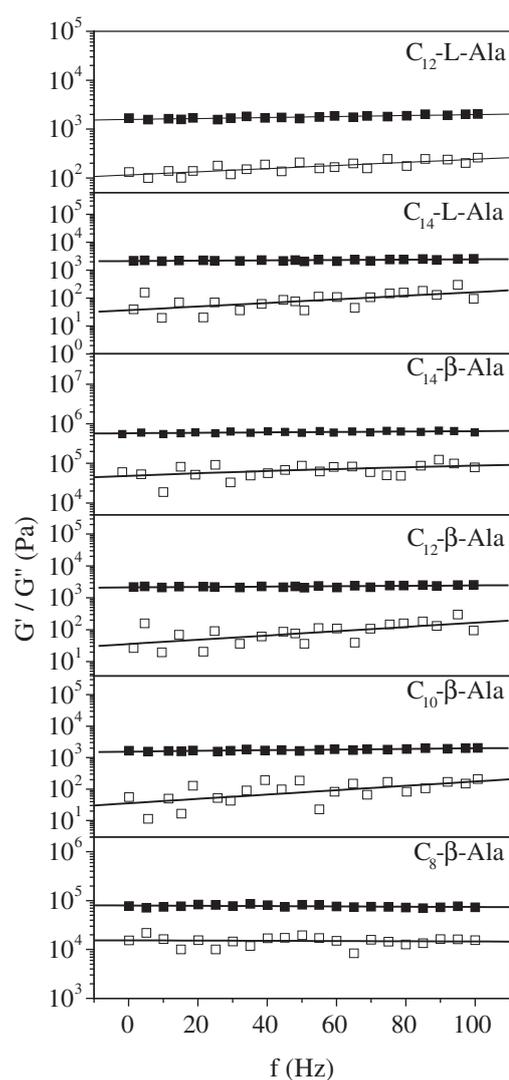


Figure 4. Plot of storage (G' , \blacksquare) and loss (G'' , \square) moduli of the organogels containing 0.15 M C_n - β -Ala or C_n -L-Ala in p -Ph(Me)₂ as a function of frequency (f).

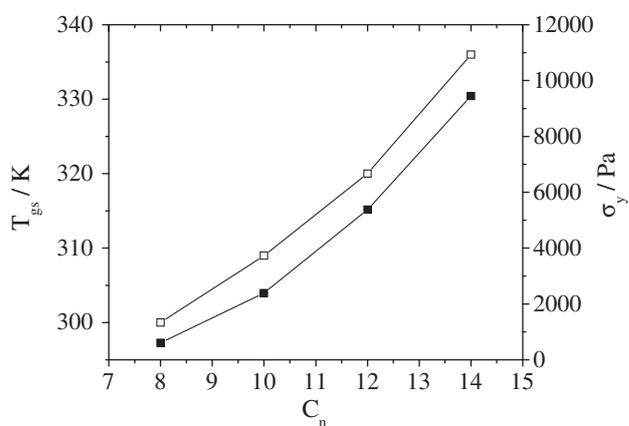


Figure 5. Plots of T_{gs} (\square) and σ_y (\blacksquare) of the organogels in p -Ph(Me)₂ versus hydrocarbon chain length (C_n) of the gelators; T_{gs} was determined with samples containing 0.05 M gelator.

process does not necessarily lead to gelation. The role of van der Waals interaction cannot be neglected as the gelation ability is

observed to increase with the increase of hydrocarbon chain length. The van der Waals interactions between hydrocarbon tails facilitate one-dimensional growth of the aggregate. Indeed strong interaction between hydrocarbon chains is indicated by the band at 1456 cm^{-1} in the FT-IR spectrum of the gelators [25]. Also, probably the nanofibers thus formed are entangled with each other through van der Waals interaction.

2.3. Role of chiral center

In order to investigate the role of chiral center, we also studied the gelation properties of C_{12} -L-Ala and C_{14} -L-Ala. For comparison purposes, the results are included in Table 1. The data in Table 1 show that C_n - β -Ala gels only aromatic solvents in contrast to C_{12} -L-Ala and C_{14} -L-Ala that gel aliphatic as well as aromatic hydrocarbons [14,15]. This might be due to the difference in hydrophobicity of the amino acid head group. The head group of the C_n -L-Ala amphiphile being more hydrophobic interacts favorably with the less polar aliphatic hydrocarbon solvents. That the head group hydrophobicity is important is shown by the fact that N-acyl glycine (C_n -Gly) amphiphiles failed to gel organic solvents [14]. Also it is important to note that in any solvent the CGC values of C_{12} -L-Ala and C_{14} -L-Ala are slightly less than that of corresponding C_n - β -Ala gelators, suggesting that chirality enhances gelation ability. In other words, chirality plays an important role in self-organization of the gelator molecules. Indeed it is well known that 'chiral bilayer effect' enhances 1-D growth of the self-assembled aggregates, forming fibers [27]. In fact, the affinity between chiral molecules has been experimentally verified with amino acids that form large aggregates from enantiopure substrates than from racemic ones [28]. This means enantiopure amino acids favor formation of homochiral aggregates (in which all the constituent units are of the same chiral form). This is because it reduces entropy barriers in the formation of large organized molecules. Indeed it is well known that when racemic sodium chlorate is allowed to crystallize from aqueous solution each crystal turns out to be either L-form or D-form [29]. Further enantiopure molecules are known to pack better in the crystal. This is why an enantiopure compound has melting (or boiling) point higher than that of corresponding racemic compound.

The poor solubility of C_{14} - β -Ala in organic solvents indicates that gelator-gelator intermolecular interactions are stronger than in C_n -L-Ala gelators. This is manifested by the *mp* of the solid gelators; the C_{14} - β -Ala amphiphile has *mp* (405 K) much higher than that of C_{14} -L-Ala (365 K). A similar difference in *mps* is also observed between C_{12} - β -Ala (395 K) and C_{12} -L-Ala (357 K) gelators. Since the chain length is equal in both chiral and achiral gelators, the difference in *mps* must be a consequence of the difference in H-bonding interactions. The H-bonding interaction in C_{14} -L-Ala (or C_{12} -L-Ala) is expected to be less than that in C_{14} - β -Ala (or C_{12} - β -Ala) due to steric bulk of the amino acid side chain. This means that stronger intermolecular H-bonding interaction disfavors the gel state and leads to large scale 3-D crystallization on cooling. On the other hand, the weaker H-bonding interactions of the amide and carboxylic groups in C_{14} -L-Ala (or C_{12} -L-Ala) due to the steric hindrance at the amino acid head group results in an intermediate solubility and hence favors gelation. Similar observation was also made with *N*-(*n*-tetradecylcarbamoyl)-L-alanine gelator by Dey and coworkers [17]. Perhaps in these gelators, strong H-bonding as well as affinity between chiral head groups led to large scale 3-D crystallization instead of gelation. However, in the presence of water, they produced gel due to weakening of the H-bonds. Also with *N*-(*n*-tetradecylcarbamoyl)-DL-alanine gelator, the chirality effect being eliminated gelation could be observed without the addition of water. That is for this type of gelators, chirality affects gelation process. On the other hand, affinity between chiral head

groups in C_{14} -L-Ala (or C_{12} -L-Ala) compensates weaker H-bonding between amide groups, facilitating gelation. This is supported by the phase-selective gelation of C_n -L-Ala in the presence of water. It should be noted that β -alanine-derived amphiphiles failed to exhibit phase-selective gelation in the presence of water. This is probably because H_2O molecules compete for the H-bonding sites in the gelator thus inhibiting self-association. This is substantiated by the fact that these gelators are unable to gel $CHCl_3$ in which the acidic hydrogen interacts with the amide carbonyl group [14]. This is also supported by the formation of partial gels in CCl_4 solvent, which does not have any H-bonding site. However, in the case of L-alanine gelators, although H_2O molecules break the H-bonds between amide groups, the affinity of the chiral head groups holds them together and thus exhibit phase-selective gelation. In fact, the morphology of the C_{14} -L-Ala (or C_{12} -L-Ala) organogel obtained in the presence of water remains unchanged [15]. The affinity of chiral head groups that facilitate 1-D growth of the aggregates and hence gelation ability is also manifested by the higher thermal stability of the C_{14} -L-Ala (or C_{12} -L-Ala) organogel. Indeed at a given concentration (0.05 M) greater than their CGC values, the T_{gs} value of the *p*-xylene organogels of C_{14} - β -Ala (337 K) and C_{12} - β -Ala (320 K) are less than that of C_{14} -L-Ala (342 K) and C_{12} -L-Ala (325 K), respectively.

In contrast, the mechanical strength of the C_{14} -L-Ala organogel as measured by the σ_y value (2396 Pa) was observed to be much less than that of C_{14} - β -Ala (9445 Pa) organogel in *p*-Ph(Me)₂ solvent. Similar relationship between σ_y values of the C_{12} - β -Ala (5375 Pa) and C_{12} -L-Ala (614 Pa) organogels was also observed. The higher mechanical strength of the C_{14} - β -Ala or C_{12} - β -Ala organogel is also suggested by the G'/G'' value which is greater than that of C_{14} -L-Ala (9.0) or C_{12} -L-Ala (7.5) organogels at the same gelator concentration (0.15 M) and temperature (298 K). When the micrographs (Figure 2) are compared, the morphology of the aggregates in the organogels of C_{14} - β -Ala and C_{14} -L-Ala were found to be similar. The ribbon-like aggregates of the C_{14} - β -Ala organogel is ten times thicker than that of C_{14} -L-Ala organogel. On the other hand, the aspect ratio of the ribbons in C_{12} -L-Ala organogel is much less than that of C_{12} - β -Ala organogel. Although both chiral and achiral alanine amphiphiles self-assemble to produce ribbon-like aggregates, variation in the self-assembly modes in both types of gelators is suggested by the difference in respective CGC values. This is substantiated by the XRD spectrum of C_{14} -L-Ala (Figure S6) organogel which exhibits periodic peaks corresponding to bilayer structure in which the hydrocarbon tails of the gelator molecules are not interdigitated, but the long axis is tilted with respect to the plane. This is reflected by the peak corresponding to reflection from 100 plane, which is broad and the value of long spacing (3.07 nm) is less than twice the tail length (1.77 nm).

3. Conclusions

In conclusion, we have synthesized and characterized four new β -alanine based gelators that have no chiral center at the hydrophilic amino acid headgroup. These amphiphilic gelators are shown to form organogels, but their gelation abilities are inferior to the structurally similar L-alanine-derived gelators. The results suggest that although chirality is not essential for the gelation by this class of molecules, but it is observed to enhance gelation ability and to impart thermal stability to the gel structure because of the extra affinity between chiral head groups. However, the organogels of the chiral amphiphile C_n -L-Ala was observed to have lower mechanical strength compared to corresponding C_n - β -Ala organogel, suggesting that thermal stability of the organogel is a function of the gelator-gelator intermolecular interactions and is independent of the degree of non-covalent cross-linking or entanglement of the fibrous aggregates in the 3-D network structure.

The mechanical strength of the organogels has been shown to be dependent on the van der Waals interactions between hydrocarbon chains of the amphiphilic gelators. It can be concluded that chirality can either enhance gelation or affect it depending on the molecular structure of the gelator. If the H-bonding interaction is weaker, then the affinity between chiral head groups enhances gelation ability. On the other hand, if H-bonding interaction is stronger, then the latter effect strengthens it leading to crystallization.

4. Experimental

Tetrabutylammonium fluoride (TBAF), L-alanine, β -alanine, mesitylene (Ph(Me)₃), and alkanoyl chlorides were procured from Sigma–Aldrich (Bangalore, India). The organic solvents such as *n*-hexane (*n*-C₆H₁₄), cyclohexane (C₆H₁₂), *n*-octane (*n*-C₈H₁₈), benzene (PhH), toluene (PhMe), *o*-xylene (*o*-Ph(Me)₂), *m*-xylene (*m*-Ph(Me)₂), *p*-xylene (*p*-Ph(Me)₂), chlorobenzene (Ph-Cl), nitrobenzene (PhNO₂), chloroform (CHCl₃), and tetrachloromethane (CCl₄) were of highest purity commercially available and were dried and distilled fresh before use. The C_{*n*}- β -Ala gelators were synthesized following procedure reported in the literature [16]. The details of synthesis, purification, and structural identification of the gelators are described under ESI.

In a typical gelation test, 10 mg of gelator was weighed into a 4 mL screw-capped vial (8 mm o.d.), organic solvent was added and then heated in a hot water bath to completely dissolve the solid. The resulting dispersion was then kept in a temperature controlled water bath at 298 K for cooling; gelation was confirmed when the material did not flow upon inversion of the vial. The gelation was observed in less than 30 min. The heating–cooling cycle was repeated for every addition of solvent. CGC was determined from the maximum volume of solvent taken by a known mass of the gelator. Gel-to-sol transition temperature was determined by heating the organogel slowly (1 °C/min) in the water bath; melting was checked by tilting the vial from time to time.

Description of different physical methods used for the work can also be found under ESI.

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Appendix A. Supplementary data

Synthesis, chemical identification of the compounds, description of experimental methods, plot of G'/G'' versus shear stress (Pa) of organogels, FTIR spectra of C₁₄- β -Ala in toluene and in chloroform, concentration-dependent ¹H NMR spectra of C₁₄- β -Ala in CCl₄ and XRD spectrum of the C₁₄-L-Ala organogel in *p*-xylene solvent are available free of charge via the Internet.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2012.10.089>.

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