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PAPER

Rheology and thermal stability of pH-dependent hydrogels of *N*-acyl-L-carnosine amphiphiles: effect of the alkoxy tail length†

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A series of L-carnosine derived organogelators, *N*-(4-*n*-alkoxybenzoyl)-L-carnosine (C_n OBC, where $n = 6-16$ denotes the number of carbon atoms in the alkoxy tail), were synthesized to elucidate the effect of hydrophobic interaction on their gelation abilities in water and gel–sol melting temperatures. The variation of pH-responsiveness, morphology, and mechanical strength of the hydrogels with the change of the alkoxy tail length has been studied. The thermal stability and gelation ability were observed to increase linearly with the alkoxy tail length. Both thermal stability and mechanical strength were observed to be highest with the C_{16} OBC gelator. Although thermal stability of the hydrogels of any gelator was highest at pH 2, the yield stress of the corresponding gel was highest at pH 7. The mechanical strengths of the hydrogels were observed to decrease sharply with the increase of pH above 7. All the gelators self-assembled to form ribbon-like aggregates consisting of interdigitated bilayers, which suggest that van der Waals interaction between hydrocarbon chains is the dominant driving force for aggregate formation.

Introduction

Hydrogels are soft materials that have attracted special attention from the pharmaceutical industry due to a large variety of applications in cosmetics, pharmaceuticals, and biomedicines.^{1–4} Since hydrogels contain a large volume fraction of water, they are ideal candidates for protein delivery. The three dimensional (3D) network structures of hydrogels allow the protein to be retained in the active form and also prevent them from becoming denatured during administration. For efficient drug delivery, hydrogels have been developed, whose network structures respond to changes in stimuli, such as temperature, pH, light, *etc.* Among these stimuli, pH is an important stimulus for transdermal drug delivery and for cancer treatment. It is well known that the pH of the skin is in the range of 5–6. On the other hand, most damaged tissues (*e.g.*, cancer) usually have lower pH (4.5–6.5). Therefore, pH has been taken into account in designing responsive physical gels for biomedical applications. Physical gels are also thermoresponsive. Drug delivery systems based on hydrogels obtained from molecular gelators (MGs), which are low-molecular-weight organic compounds, have become more interesting due to their biodegradability. However, in

comparison to gelators that gel organic solvents, there are not many MGs that are capable of forming hydrogel. Nonetheless, a number of MGs are known in the literature^{5–12} that gel water. Examples of such MGs include urea,⁵ amino acid,^{6,7} peptides⁸ and nucleobase derivatives,⁹ bis-oxalyl amides,¹⁰ gemini surfactants,¹¹ and also sugar amphiphiles.¹² Hydrogels based on mixed systems have also been reported.¹³

Among these MGs, amino acid and peptide based gelators are finding importance because of their potential biocompatibility and applications in drug delivery, tissue engineering, and cell culture.¹⁴ These peptide hydrogels are known to form through various supramolecular structural motifs such as α -helix, β -sheet, β -hairpin, coiled coil, and so on.¹⁵ It is often observed that a small peptide or an amino acid with modified C- and N-terminal groups by either an aromatic ring or a long alkyl chain can self-assemble to form supramolecular gels.¹⁶ Recently, we have reported pH-sensitive hydrogel formation by *N*-(4-*n*-tetradecyl-oxybenzoyl)-L-carnosine at a relatively low concentration.¹⁷ L-Carnosine is a dipeptide that consists of two amino acids, L-histidine and β -alanine. The *N*-(long-chain-acyl)-L-carnosine derivatives are known to have excellent emulsifying activity. These amphiphilic molecules also possess antioxidant activity toward lipid peroxidation.¹⁸ Previously we have investigated the effect of pH, salt (NaCl), and alcohol on the gelation behavior of the *N*-tetradecyloxybenzoyl derivative of the *N*-acyl dipeptide.¹⁷ Due to responsiveness to change in temperature, pH, and ionic strength, these kinds of smart molecules are very good candidates for designing hydrogels for biomedical applications.

It is well-known that gelation is a result of a subtle self-assembly process due to the combined effect of non-covalent

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† Electronic supplementary information (ESI) available: MGC values of the gelators, X-ray diffraction patterns, 2θ values and the corresponding interlayer distance of the hydrogels, plot of G'/G'' versus frequency and stress amplitude of the hydrogels in different pHs. See DOI: 10.1039/c1sm06209c

interactions, e.g., ion–ion, dipole–dipole, hydrogen-bonding (H-bonding), π – π stacking, van der Waals, and solvophobic interactions between molecular gelators to produce fibrillar structures. The subsequent entanglement or non-covalent crosslinking of these fibrils leads to the formation of a 3D network of supramolecular fibers that immobilize solvent, resulting in gelation. It should, however, be noted that it is not the fibril formation but the formation of solvated fibrils which is a necessary prerequisite for gelation. Among other factors (e.g., solvent, concentration, additive, and temperature) that influence the self-assembly process, the molecular architecture of the gelator is very important.^{1–4} A minimal structural variation may lead to significant changes of molecular aggregate morphology and hence gelation ability. The length of the flexible tail of an amphiphilic gelator can be used as a structural parameter to manipulate the morphology of the gel and gelation ability of the organogelators.^{19–23} For some gelators, an increase of the tail length enhances gelation ability.²⁰ In contrast, in the case of *N*-acyl-L-alanine and L-valine amphiphiles, although gelation ability increases initially with the increase of the chain length up to C14, increasing chain length thereafter weakens gelation ability.²¹ A similar observation was also made with *N*-alkyl perfluoroalkanamides.^{22,23} On the other hand, in the case of arjunolic acid, gelation ability decreases in aromatic solvents but increases in aliphatic hydrocarbon solvents with the increase of the chain length.²³ This suggests that there is an inherent relationship between non-covalent interactions and the gelation ability of a gelator. For most amphiphilic MGs that have two parts, one hydrophilic head (or aromatic moiety) and a hydrophobic tail, the variation of sol–gel transition temperature (T_{gs}) and gelation ability as a result of the change of the hydrocarbon tail length is relatively simple. However, the situation becomes more complicated when additional interactions, such as π – π stacking interactions, are also involved. It has been proposed that the self-assembly of hydrogelators is driven by the hydrophobic effect as well as by the van der Waals interaction between hydrocarbon chains.

The present work was undertaken to understand the effect of the hydrophobic interaction in hydrogelation by amphiphilic MGs. The aim of the present study is to investigate the effects of the alkoxy tail length and pH on the gelation ability, thermal stability, morphology, and mechanical strength of the hydrogels of the *N*-acyl derivatives of L-carnosine. For this, a series of *N*-(4-*n*-alkoxybenzoyl)-L-carnosine (C_n OBC, where $n = 6–16$ denotes the number of carbon atoms in the alkoxy tail) amphiphiles, were synthesized. The series of amphiphiles examined are related structurally with the intermolecular interactions responsible for gelation in a systematic way through varying the length of the alkoxy tail. We are interested in investigating the correlation between the tail length and thermal stability, morphology, and mechanical strength of the hydrogels formed by these MGs. The hydrogels at different pHs were studied by FTIR and NMR spectroscopy, scanning electron microscopy, XRD, and rheology.

Experimental section

Materials

4-Hydroxybenzoic acid, 1-bromododecane, 1-bromodecane, 1-bromooctane, and anhydrous potassium carbonate, sodium

bicarbonate, *N*-hydroxysuccinimide (NHS), 1,3-dicyclohexylcarbodiimide (DCC), sodium hydrogen carbonate, sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium acetate, sodium borate, hydrochloric acid, and sodium hydroxide were purchased from SRL, Mumbai, India, and were used without further purification. 1-Bromohexadecane, 1-bromotetradecane, hexyloxybenzoyl chloride and L-carnosine were obtained from Aldrich. All the organic solvents were of the highest purity commercially available and were dried and distilled fresh before use. Milli Q water was used for the preparation of buffers. All the amphiphiles employed in this study were synthesized in the laboratory as described below.

Synthesis of amphiphiles

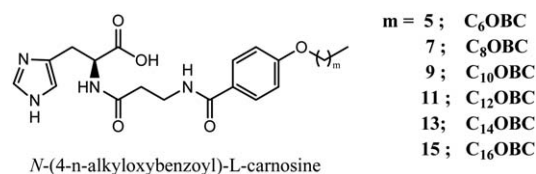
N-(4-*n*-Alkoxybenzoyl)-L-carnosine amphiphiles (Chart 1) were synthesized following a procedure described elsewhere.¹⁷ The compounds were purified by recrystallization from ethanol–water mixture. For *N*-(4-*n*-hexyloxybenzoyl)-L-carnosine (C_6 OBC), L-carnosine was directly reacted with hexyloxybenzoyl chloride in THF/ H_2O mixture in the presence of triethylamine (pH 8–9). Chemical identification of all the compounds was performed by use of 1H NMR, FT-IR spectroscopy and elemental analysis.

Chemical identification of the amphiphiles

C_6 OBC. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +24.264, 1H NMR (200 MHz, D_2O , NaOD) δ (δ in ppm): 0.76 (t, 3H, $CH_2(CH_2)_6CH_3$), 1.19 (m, 12H, $CH_2(CH_2)_4CH_3$), 1.51 (t, 2H, OCH_2CH_2), 2.47 (t, 2H, $COCH_2CH_2NH$), 3.04 (d, 2H, CH_2CHNH), 3.50 (q, 2H, $CO-CH_2CH_2-NH-$), 4.38 (q, 1H, $CH_2-CH-NH$), 6.7 (s, 1H, imidazole CH), 7.2 (d, 1H, benzene ring), 7.5 (s, 1H, imidazole N-CH-NH), 7.7 (d, 1H, benzene ring), FT-IR (KBr, cm^{-1}): 2852–2921, 3297, 1542, 1636, 1701, 1250 CHN analysis: C 55.5%, H 7.13%, N 13%.

C_8 OBC. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +18.416, 1H NMR (400 MHz, CD_3OD) δ (δ in ppm): 0.90 (t, 3H, $CH_2(CH_2)_6CH_3$), 1.32 (m, 12H, $CH_2(CH_2)_6CH_3$), 1.77 (t, 2H, OCH_2CH_2), 2.53 (t, 2H, $-CO-CH_2-CH_2-NH$), 3.04 (d, 2H, CH_2CHNH), 3.23 (q, 2H, $CO-CH_2CH_2-NH-$), 4.56 (q, 1H, CH_2CHNH), 6.9 (s, 1H, imidazole CH), 7.1 (d, 1H, benzene ring), 7.7 (s, 1H, imidazole NCHNH), 7.9 (d, 1H, benzene ring). FT-IR (KBr, cm^{-1}): 2853–2924, 3298, 1541, 1630, 1710, 1251 CHN analysis: C 56.64%, H 7.5%, N 12.1%.

C_{10} OBC. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +19.06, 1H NMR (200 MHz, D_2O , NaOD) δ (δ in ppm): 0.816 (t, 3H, $CH_2(CH_2)_8CH_3$), 1.22 (m, 16H, $(CH_2)_8CH_3$), 1.45 (t, 2H, OCH_2CH_2), 2.36 (t, 2H, $COCH_2CH_2NH$), 2.73 (t, 2H, CH_2CHNH), 3.15 (q, 2H, $COCH_2CH_2NH$), 4.3 (q, 1H, CH_2CHNH), 6.79 (s, imidazole



N-(4-*n*-alkoxybenzoyl)-L-carnosine

Chart 1 Chemical structures of *N*-(4-*n*-alkoxybenzoyl)-L-carnosine amphiphiles.

CH), 7.56 (d, 1H, benzene ring), 7.75 (s, 1H, imidazole NCHNH), 8.13 (d, 1H, benzene ring), FT-IR (KBr, cm^{-1}): 2853–2923, 3296, 1545, 1635, 1706, 1250 CHN analysis: C 58.8%, H 6.99%, N 11.5%.

$C_{12}OBC$. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +20.76 ^1H NMR (400 MHz, D_2O , NaOD) δ (δ in ppm): 0.75 (t, 3H, $\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.12 (m, 12H, $\text{CH}_2(\text{CH}_2)_6\text{CH}_3$), 1.43 (t, 2H, OCH_2CH_2), 2.33 (t, 2H, $-\text{CO}-\text{CH}_2-\text{CH}_2-\text{NH}$), 2.81 (d, 2H, CH_2CHNH), 3.29 (q, 2H, $\text{CO}-\text{CH}_2\text{CH}_2-\text{NH}$), 4.26 (q, 1H, CH_2CHNH), 6.51 (s, 1H, imidazole CH), 6.59 (d, 1H, benzene ring), 7.19 (s, 1H, imidazole NCHNH), 7.48 (d, 1H, benzene ring). FT-IR (KBr, cm^{-1}): 2852–2926, 3297, 1546, 1631, 1708, 1254 CHN analysis: C 60.1%, H 8.12%, N 10.9%.

$C_{14}OBC$. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +19.50, ^1H NMR (200 MHz, D_2O , NaOD) δ (δ in ppm): 0.74 (t, 3H, $\text{CH}_2(\text{CH}_2)_{12}\text{CH}_3$), 1.32 (m, 24H, $(\text{CH}_2)_{12}\text{CH}_3$), 1.99 (t, 2H, $\text{COCH}_2(\text{CH}_2)_{12}\text{CH}_3$), 2.75 (t, 2H, $\text{COCH}_2\text{CH}_2\text{NH}$), 3.41 (q, 2H, $\text{COCH}_2\text{CH}_2\text{NH}$), 4.28 (q, 1H, CH_2CHNH), 6.5 (s, imidazole CH), 6.6 (d, 1H, benzene ring), 7.5 (s, imidazole NCHNH), 7.54 (d, 1H, benzene ring), FT-IR (KBr, cm^{-1}): 2852–2924, 3295, 1542, 1639, 1711, 1256 CHN analysis: C 61.5%, H 8.1%, N 10.3%.

$C_{16}OBC$. $[\alpha]_D^{25}$ (0.5%, CH_3OH) = +18.78, ^1H NMR (200 MHz, D_2O , NaOD) δ (δ in ppm): 0.76 (t, 3H, $\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$), 1.2 (m, 28H, $(\text{CH}_2)_{14}\text{CH}_3$), 1.92 (t, 2H, $\text{COCH}_2(\text{CH}_2)_{14}\text{CH}_3$), 2.56 (t, 2H, $\text{COCH}_2\text{CH}_2\text{NH}$), 3.11 (q, 2H, $\text{COCH}_2\text{CH}_2\text{NH}$), 4.29 (q, 1H, CH_2CHNH), 6.57 (s, imidazole CH), 6.6 (d, 1H, benzene ring), 7.25 (s, imidazole N–HNH), 7.52 (d, 1H, benzene ring), FT-IR (KBr, cm^{-1}): 2854–2927, 3295, 1545, 1638, 1712, 1252 CHN analysis: C 62.9%, H 8.3%, N 9.82%.

Methods and instrumentation

The melting point of solid compounds was measured using Instind (Kolkata) melting point apparatus with open capillaries. The measurements of optical rotations were performed with a JASCO (Model P-1020) digital polarimeter. The FTIR spectra were measured with a Perkin-Elmer (Model Spectrum Rx I) spectrometer. The ^1H NMR spectra were recorded on an AVANCE DAX-400 (Bruker, Sweden) 400 MHz NMR spectrometer in CD_3OD or $\text{D}_2\text{O}/\text{NaOD}$ solvent with CH_3CN as a standard. All measurements were done at 298 K unless otherwise mentioned.

Aqueous buffers (20 mM) in the pH range of 3–11 were used for the gelation studies. Buffers of pH 3, 6, 7, and 8 were made by mixing appropriate volumes of 0.2 M NaH_2PO_4 , Na_2HPO_4 , and HCl (or NaOH) solutions. Acetate buffers were used for pH 4 and 5. On the other hand, borate buffers were employed for pH 9 and 10. The pH 1 and 2 solutions were made directly from the HCl solution. The ionic strength of all the buffer solutions was adjusted to 0.1 by adding an appropriate volume of 0.5 M NaCl solution.

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

The XRD spectra were taken at room temperature for all air-dried hydrogel samples prepared on a glass slide. The experiment

was performed on a Pan analytical X'Pert pro X-ray diffractometer using Cu target (Cu $K\alpha$) and Ni filter at a scanning rate of 0.001 s^{-1} between 2 and 12° , operating at a voltage of 40 kV and current 30 mA.

Rheology measurements were performed on a Bohlin RS D-100 (Malvern, UK) rheometer using parallel-plate (PP-20) geometry. The gap between the plates was fixed at 100 μm . The hydrogel was placed on the rheometer and a stress-amplitude sweep experiment was performed at a constant oscillation frequency of 1.0 Hz at 25°C .

Results and discussion

Gelation studies

The gelation ability of the amphiphiles was tested in the 20 mM buffer solution of different pHs (pH 1 to 12). Heating the gelator at pH 7 gives an aqueous dispersion, which on cooling at 298 K for an hour gives an opaque hydrogel. The gelation occurred just by one or two alternate heating and cooling cycles. For long chain amphiphiles, *i.e.* $C_{14}OBC$ and $C_{16}OBC$, strong heating for a longer time was needed for the solubilization of the compounds. At room temperature and at a gelator concentration close to the “minimum gelator concentration” (MGC, defined as the minimum amount (mg) of gelator required to gelate 1 mL of solvent at a given temperature), it took 1–3 hours for the gelation to take place. The gel formation of the amphiphiles in buffers was confirmed by simple tube inversion experiments. The mixture which remained in position after tube inversion is described as a gel here. It should be noted that the amphiphiles failed to gelate buffers in the pH range of 3–6. The longer chain length amphiphiles remain insoluble and the amphiphiles with shorter hydrocarbon chain either result in an optically opaque dispersion or precipitate upon cooling to 298 K. All the gelators were found to gelate water in both alkaline ($7.0 \leq \text{pH} \leq 11.0$ or ≤ 10) and moderate acidic ($0.3 \leq \text{pH} \leq 2$ or only at pH 2) pH regimes. The gelation was observed to be thermoreversible at all pHs. The hydrogels thus formed by the amphiphiles remained unchanged for months when preserved under constant condition of pH and temperature (298 K).

Influence of pH and hydrocarbon chain length on the gelation

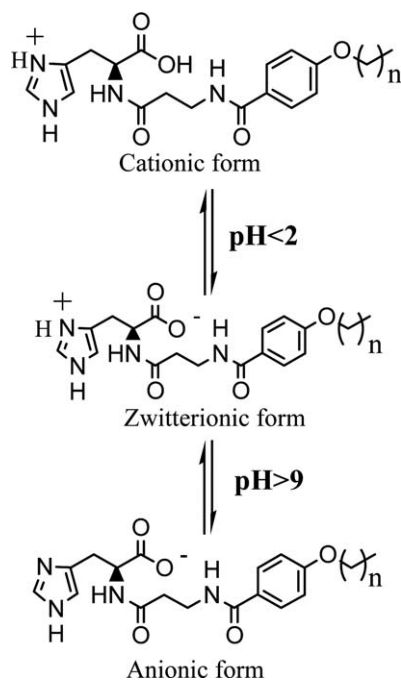
The gelation ability of the amphiphiles was quantitatively evaluated by determining the “gelation number,” N_{gel} which is the mole ratio of entrapped solvent to gelator. In other words, N_{gel} is the maximum number of solvent molecules that are immobilized by a molecule of the gelator. The N_{gel} values have been listed in Table 1. The N_{gel} values were calculated from the measured MGC values using the molar mass of the gelator and density (0.997 g mL^{-1}) of water at 298 K. The molar masses of the gelators and the MGC values can be found in Table S1 of the ESI†. The gelation number is relatively high, suggesting good gelation ability of the amphiphiles at neutral pH. For any gelator, the N_{gel} value was observed to be highest at neutral pH. However, both a decrease and increase of pH cause reduction of the N_{gel} value. The pH effect can be explained by the protonation equilibria of the amphiphiles in water as reported in our earlier publication.¹⁷ Briefly, the gelator molecule exists in three different forms, cationic, zwitterionic and anionic at different

Table 1 Gelation number (N_{gel}) of the hydrogels of $C_n\text{OBC}$ gelators at different pHs at 298 K; the quantities within parentheses represent gel melting temperatures (T_{gs}/K) of the gelators (0.02 M)^b

pH	N_{gel} (T_{gs}/K)					
	$C_6\text{OBC}^a$	$C_8\text{OBC}$	$C_{10}\text{OBC}$	$C_{12}\text{OBC}$	$C_{14}\text{OBC}$	$C_{16}\text{OBC}$
1	P	P	P	P	4600	5125
2	2425	3171	3688 (333)	4067 (338)	5429 (344)	6340 (349)
7	2725	4879 (323)	5384 (328)	5931 (334)	8882 (338)	10 630 (343)
8	2396	4612 (321)	5127 (326)	5582 (332)	6254 (337)	10 454 (341)
9	2216	4374 (319)	4985 (325)	5176 (330)	5488 (335)	9567 (339)
10	1677	4092 (318)	4377 (323)	4761 (329)	4954 (333)	9286 (337)
11	D	D	D	4126 (327)	4358 (330)	5315 (333)

^a Gelation studies for this amphiphile were done at 15 °C.
^b P: Precipitation, D: Dispersion.

pHs (Scheme 1). In the acidic pH or basic pH range, the compound remains charged *i.e.*, either cationic or anionic, causing interionic repulsion between the similarly charged molecules in the aggregates. So the gelator–gelator interaction gets weakened and gel formation occurs with a lower N_{gel} value. The failure of gelation by $C_6\text{OBC}$, $C_8\text{OBC}$, and $C_{10}\text{OBC}$ at pH 11 clearly suggests the role of hydrophobic and van der Waals interactions of the hydrocarbon chains. These attractive interactions were weaker compared to electrostatic repulsion of the ionic headgroups at pH 11, which prevented 1D growth of the self-assemblies. But at neutral pH, the gelator molecule exists in



Scheme 1 Proton transfer equilibria of $C_n\text{OBC}$ at higher and lower pHs.

electrically neutral zwitterionic form. The distance between the gelator molecules is suitable to cause all the intermolecular interactions, *i.e.*, H-bonding, π – π stacking, and hydrophobic interaction between them. Thus the gel formation occurs with a relatively large value of N_{gel} . The failure to form gels at pH > 11 might be due to the large concentration of OH^- ion that disrupts amide H-bonds in the self-assembled structure.

In order to examine the effect of the hydrocarbon chain length on the hydrogel formation, a gelation test was performed with all the amphiphiles. The gelator $C_6\text{OBC}$ gels water at a temperature (≤ 293 K) slightly lower than room temperature. Also it was observed that $C_6\text{OBC}$ produced a weaker hydrogel, which started to flow upon gentle shaking. The data in Table 1 show that $C_{16}\text{OBC}$ has the highest value of N_{gel} at any given pH; that is, in contrast to literature reports,^{21–23} the gelation ability continuously increases with the increase of the alkoxy tail length. This is shown by the data in Table 1. This can be explained by the fact that with the increase of the chain length, both the hydrophobic effect and van der Waals interactions between the alkoxy tails increase linearly. Indeed, the increase of molecular packing (*i.e.*, ΔH_m) with the alkyl chain length, as reported elsewhere,²⁴ is linear. The contribution to the van der Waals interaction by each $-\text{CH}_2-$ group in the chain is observed to be equal to 3.5–4.2 kJ mol⁻¹ in water.²⁴ This increase of anisotropic interaction favors 1D growth of aggregates, which by physical entanglement results in a 3D network structure, in which a large number of water molecules can be entrapped, causing gelation with a higher value of N_{gel} .

Morphology of the hydrogels

In order to confirm gelation in water, the morphology of the air-dried gels of $C_{16}\text{OBC}$, $C_{14}\text{OBC}$, $C_{12}\text{OBC}$, $C_{10}\text{OBC}$, $C_8\text{OBC}$, and $C_6\text{OBC}$ was investigated by the FE-SEM technique. The FE-SEM images (Fig. 1) of the dry gels exhibit a 3D network structure of ribbon-like aggregates confirming gel formation. The images at both pH 2 and 8 clearly show that the amphiphiles are self-assembled into ribbons of high aspect ratio, which are bilayer assemblies of the gelating molecules. Although the aggregate morphology is similar at both acidic and basic pH, the aspect ratio of the ribbons seems to be different. Indeed the micrograph of the organogel of $C_{16}\text{OBC}$ amphiphile at pH 11 reveals fibrous aggregates of much lower aspect ratio. This has been discussed below under viscoelastic behavior.

The formation of bilayer self-assemblies was also confirmed by the X-ray diffraction patterns (Fig. S1 of the ESI†) of the gel cast film, which exhibit periodical reflection peaks. The peak positions (2θ values) for all the hydrogels are listed in Table S2 of the ESI†. The relative peak position $q_1 : q_2 : q_3 : q_4$ is 1 : 2 : 3 : 4, which is typical for a Bragg scattering pattern from a 1D lamellar structure. In the case of $C_6\text{OBC}$ (pH 2 and 8), $C_8\text{OBC}$ (pH 2 and 8), $C_{10}\text{OBC}$ (pH 8), $C_{12}\text{OBC}$ (pH 2 and 8), $C_{14}\text{OBC}$ (pH 2 and 8) and $C_{16}\text{OBC}$ (pH 2 and 8), there exists repetition of planes. This means that gelator molecules self-assemble into an ordered lamellar structure. The bilayer thickness of the amphiphiles and the corresponding planes are also listed in Table S2†. The extended length of the hydrophobic tail of the gelators as obtained from geometry optimization by MM2 calculation using ChemDraw Ultra 7 software have also been included in the table.

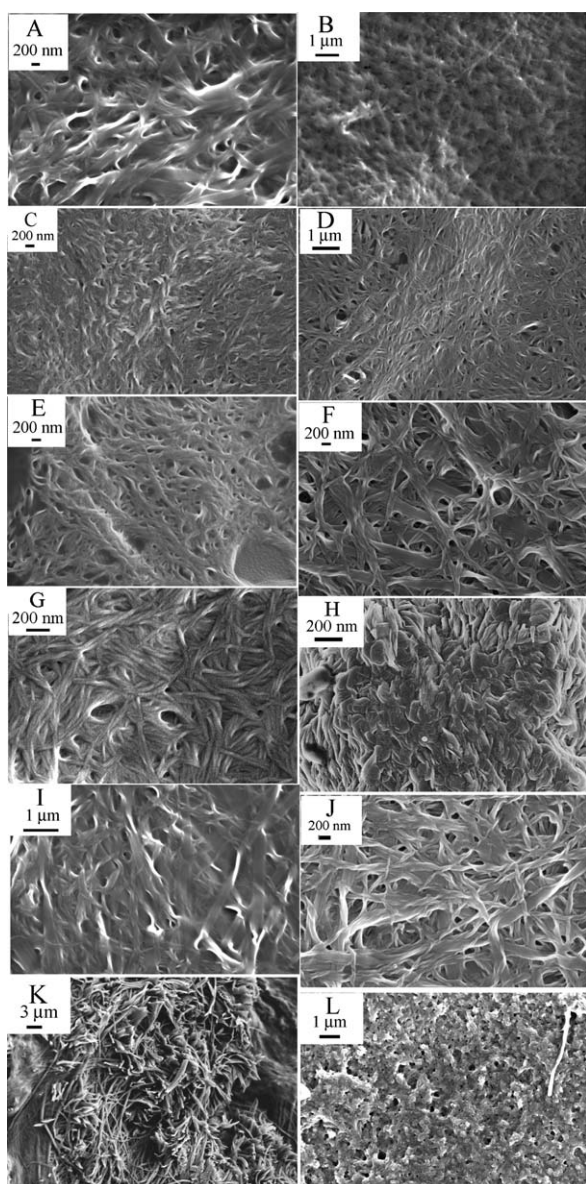


Fig. 1 FESEM images of the dried gels of (A) C_6 OBC at pH 2, (B) C_6 OBC at pH 8, (C) C_8 OBC at pH 2, (D) C_8 OBC at pH 8, (E) C_{10} OBC at pH 2, (F) C_{10} OBC at pH 8, (G) C_{12} OBC at pH 2 (H) C_{12} OBC at pH 8, (I) C_{14} OBC at pH 2, (J) C_{14} OBC at pH 8, (K) C_{16} OBC at pH 8 and (L) C_{16} OBC at pH 11.

The bilayer thickness of the amphiphiles is smaller than twice the extended length of the hydrophobic tail of the molecule, but larger than the length of the hydrophobic tail. This means that the bilayer assembly is constituted by the interdigitated hydrocarbon tails of the gelator molecules, which facilitate H-bonding interactions at the headgroup of the amphiphile. The combined effect of these interactions leads to an anisotropic growth of the lamellar structure forming ribbons.

Driving force for aggregate formation

The driving force for the gelation process was investigated by the use of NMR spectroscopy. The temperature dependent ^1H NMR spectra of C_{14} OBC (10 mg mL^{-1} *i.e.* 0.018 M in D_2O) are shown

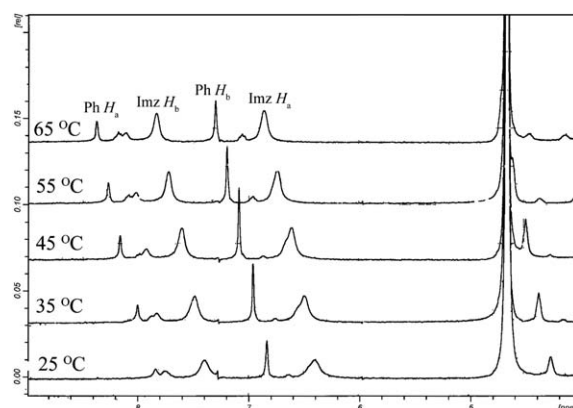


Fig. 2 Temperature dependent chemical shift (δ_{H} in ppm) of phenyl proton and imidazole (Imz) proton in 0.018 M C_{14} OBC gel in 20 mM phosphate buffer of pH 7.

in Fig. 2. A strong van der Waals interaction is also indicated by the broad peak (not shown) due to the hydrocarbon chain ($-\text{CH}_2-$) protons. The π - π stacking interaction could be confirmed from the change in chemical shift values of the phenyl as well as imidazole ring protons. From Fig. 2, it is observed that the aromatic proton peaks (H_a and H_b for Ph-H and N-CH-C and N-CH-N for Imz-H) exhibit a downfield shift with the increase of temperature. The ^1H NMR spectrum of the phenylic proton displays a broad signal even at elevated temperature, whereas that for imidazole proton displays a sharp signal. The δ_{H} values of both types of protons are observed to shift toward downfield positions linearly (Fig. 3) with the increase in temperature. The increase of δ_{H} value with the increase of temperature suggests a change in the microenvironment of the amphiphiles due to loss of H-bonding and π - π stacking interactions at higher temperatures. The proton signal from the $-\text{COOH}$ group and $-\text{CONH}_2$ group could not be observed due to a rapid chemical exchange in D_2O . However, the inter-molecular amide H-bonding interaction between *N*-acyl amino acid amphiphiles in their self-assembly formation in water is well known.²⁵

At room temperature, *i.e.*, at $25 \text{ }^\circ\text{C}$, in the gel state, the ring current of the π electron in the aromatic ring is disturbed due to

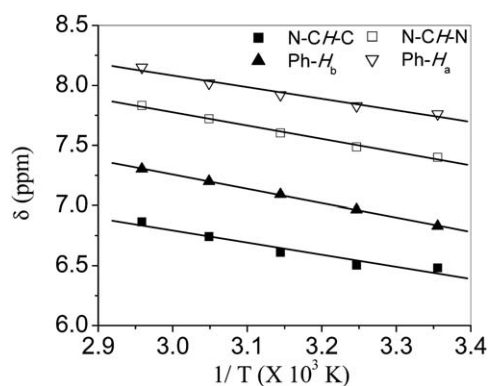


Fig. 3 Temperature dependent chemical shift (δ_{H} in ppm) of phenyl proton (Ph- H_a and Ph- H_b) and imidazole proton (N-CH-C and N-CH-N) in 0.018 M C_{14} OBC gel in 20 mM phosphate buffer of pH 7.

the π - π interaction. As a result the resultant paramagnetic field is less and the aromatic proton appears in a somewhat high field. But when the temperature is increased, the gel turns to sol and the π - π stacking interaction is weakened. As a result, the delocalisation of π electron occurs in a proper manner, causing a downfield shift of the aromatic protons.

Thermal stability

Thermal stability of the hydrogels was investigated by the inverted-tube method. To compare the thermal stability, gel melting temperature (T_{gs}) for a known concentration (0.02 M) of each of the gelators was measured. The T_{gs} values of all the amphiphiles at a concentration of 0.02 M at different pHs are listed in Table 1. The hydrogels indicated melting in the temperature range of 301–349 K. Above this temperature the gelled mass started to flow and changed to sol form. A representative plot of the variation of T_{gs} versus pH in the case of $C_{14}OBC$ at a particular concentration (0.02 M) is shown in Fig. 4. It is observed that the hydrogel at pH 2 has the highest melting temperature, suggesting its highest stability in acidic pH. The gel melting temperature, however, decreases slightly with the increase of pH above 7.0. It is interesting to observe that the gel melting temperature increases linearly with the increase of the chain length (Fig. 5). Thus at a given pH, the hydrogel of $C_{16}OBC$ has the highest T_{gs} value. This is consistent with the variation of the N_{gel} value upon increase of the alkoxy tail length.

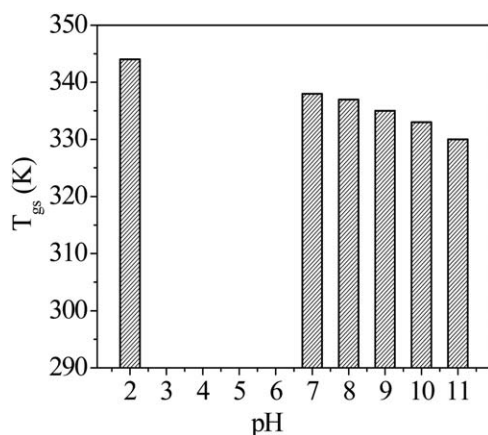


Fig. 4 Plot of T_{gs} (K) of $C_{14}OBC$ (0.02 M) as a function of pH.

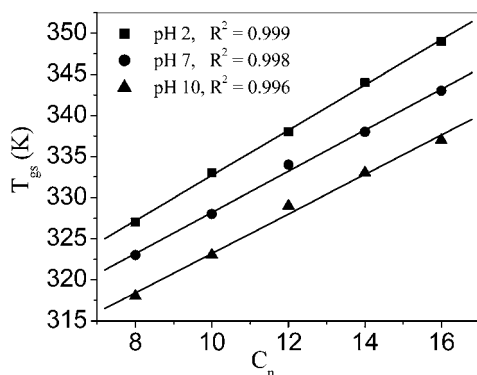


Fig. 5 Variation of T_{gs} (K) with the hydrocarbon chain length (C_n).

Viscoelastic behaviour

An oscillatory frequency sweep experiment was performed to examine the mechanical strength of the hydrogels. The linear viscoelastic regime (0.1 to 1%) was first determined from a strain sweep analysis. Therefore, all the frequency sweep experiments were conducted between 0.1 and 100 Hz within the linear regime (Fig. S2 of the ESI†). The rheology was performed with the hydrogel of all the amphiphiles (0.02 M) at pH 2 and pH 7 at 298 K. The storage (G') and the loss (G'') moduli, which characterize the strength of gels, were found to be independent of frequency. This is consistent with the formation of rigid hydrogels. Also in all the cases, the G' and G'' values were almost an order of magnitude apart which demonstrates the dominant elastic behaviour of the system and hence establishes gelation. It can be concluded that the rheological behaviour of the hydrogels is characteristic of soft viscoelastic solids.

An oscillatory strain sweep was also conducted for all the hydrogels in order to determine the point at which the supra-molecular network structure collapses. The strain sweep experiments were performed at 0.1–100% strain with a constant frequency of 10 Hz. The sample yielded at strains greater than 1% as shown by the plots of G' (Fig. S3†) as a function of stress. The characteristic feature of the plots suggests that gels start to flow above a critical stress, which is defined as the “yield stress”. The “yield stress” (σ_y) at which the gel breaks under the applied force and begins to flow is given in Table 2. It has been noted that the σ_y value is greater at pH 7 than that at pH 2 and pH 11, while the T_{gs} value follows the order pH 2 > pH 7 > pH 11 for a hydrogel of the same concentration and same amphiphile. Thus the σ_y value is consistent with the T_{gs} value at pH 7 and pH 11, but the lower value of σ_y and higher value of T_{gs} at pH 2 indicate that though the gel is thermally stable, it is not mechanically stable to the same extent. The lower value of σ_y at pH 11 might be due to the low aspect ratio of gel fibers as suggested by the gel morphology (Fig. 1). It has also been observed that with the increase in the alkoxy tail length of the amphiphile, the σ_y value increases at all three pHs, indicating an increase of mechanical strength. The results are consistent with the variation of gelation

Table 2 The yield stress, σ_y (Pa) and the ratio of G' and G'' of the gels having concentration 0.02 M in 20 mM phosphate buffer of pH 2, pH 7 and pH 11

Compound	pH	σ_y /Pa	G'/G''	
			Amplitude sweep (at 55 Pa)	Frequency sweep (at 45 Hz)
$C_{10}OBC$	2	127	5.38	4.6
	7	1890	7.60	4.98
$C_{12}OBC$	2	401	4.55	3.48
	7	2911	10.5	5.27
$C_{14}OBC$	11	5	3.4 ^a	—
	2	636	4.44	3.71
	7	4099	4.86	6.21
$C_{16}OBC$	11	284	4.27	—
	2	1379	3.25	5.16
	7	5097	5.83	6.29
	11	409	4.55	—

^a Measurement done at a stress of 1.86 Pa.

number and gel melting temperature (Table 1) with the chain length.

Conclusions

In summary, we have demonstrated that *N*-[4-*n*-alkoxybenzoyl]-L-carnosine amphiphiles form thermo-reversible hydrogels in buffered water over a wide pH range. The gelation of water by the amphiphile occurs at concentrations less than 1% (w/v). The gelation was found to be very sensitive to pH. No gelation could be observed between pH 3 and pH 6 and at pH > 11. Among the hydrogelators, C₁₆OBC has the highest gel melting temperature at all pHs. Unlike other amphiphilic gelators reported in the literature, the gelation ability and gel melting temperature were found to be highest with C₁₆OBC due to maximum hydrophobic effect and van der Waals interactions. For any of the gelators, the gel melting temperature is highest in pH 2 and it decreases with an increase in pH. The supramolecular aggregates of the amphiphiles have ribbon-like bilayer structures, which are formed through a π - π stacking interaction of the phenyl group and van der Waals interactions of the hydrocarbon chain of adjacent molecules. The gel formed by C₁₆OBC has the highest mechanical strength at all pHs as indicated by the yield stress values which are much higher than the corresponding values of other gelators. For all the gelators, the yield stress at pH 7 is highest due to its zwitterionic character which reduces ionic repulsion between headgroups. At a pH higher or lower than 7.0 the gelation ability, thermal stability and mechanical strength are reduced due to the increased headgroup repulsion. Due to thermoreversibility and pH- and rheology-modulated hydrogelation, the amphiphiles could have potential applications in drug delivery.

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