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Self-assembled organogels formed by mono-chain L-alanine derivatives

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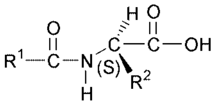
The mono-chain L-alanine derivatives self-assemble into bilayer aggregates in a number of organic liquids and gelatinize the liquids.

Recent discoveries of low molecular weight gelators have stimulated considerable interest not only in academic investigations but also technological applications.[1–9] Although dozens of different categories of gelators have so far been identified, it is difficult to select a molecule that will definitely gel a selected liquid. Previous reports reveal that some oligomers of α-amino acids[2a,b,8] and bolaform amides derived from amino acids[2c] can gel a number of organic liquids, while the reports relating mono-amino acid derivatives are relatively few.[2d,e] Bhattacharya and co-workers reported recently that mono-amino acid derivatives can gelate selectively oil from oil–water mixtures.[9] Herein, we report simple compounds, mono-chain L-alanine derivatives, which form bilayer aggregates in a number of organic liquids and gelate the liquids.

The L-alanine derivatives, **1**–**8**,† used here were prepared in our laboratory. A typical procedure for studying gel formation ability is as follows: a weighed sample was mixed with an organic liquid (1 mL) in a sealed test tube and the mixture was heated until the solid dissolved. The resulting solution was cooled at 20 °C for 2 h and then the gelation was studied. Upon formation the organogel is stable and the tube can be inverted without any change of shape of the organogel.



1 $R^1 = C_9H_{19}$, $R^2 = CH_3$
2 $R^1 = C_{11}H_{23}$, $R^2 = CH_3$
3 $R^1 = C_{13}H_{27}$, $R^2 = CH_3$
4 $R^1 = C_{17}H_{35}$, $R^2 = CH_3$
5 $R^1 = (CH_3)_3COCO$, $R^2 = CH_3$
6 $R^1 = C_6H_5$, $R^2 = CH_3$
7 $R^1 = C_{11}H_{23}$, $R^2 = H$
8 $R^1 = C_{11}H_{23}$, $R^2 = C_6H_5CH_2$

The results of gelation tests of **1**–**3** are summarized in Table 1,‡ in which the values denote the minimum gel concentrations (g L^{-1}) necessary for gelation. From Table 1, it is clear that compounds **1**–**3** can form a stable physical organogel and gelatinize a number of organic fluids even at a very low concentration. For example, the amounts of **2** necessary to gel 1 L of CCl_4, PhH, PhMe, *o*-xylene and mesitylene are 7, 4, 5, 5 and 4 g, respectively. Weiss and co-workers' studies reveal that the size of organogel colloids depends upon the nature of the liquid.[1c] The amphiphiles **1**–**3**, which form transparent or translucent organogels in different liquids, may be due to the different size of their colloids.

Table 1 Gelation test of **1**–**3** and minimum gel concentration necessary for gelation at 20 °C. Values refer to the minimum gel concentration in g L^{-1} (gelator/liquid)

	Gel concentration/g L^{-1}		
Organic liquids	1	2	3
Carbon tetrachloride	6 (translucent)	7 (translucent)	6 (translucent)
Benzene	5 (transparent)	4 (transparent)	4 (transparent)
Toluene	5 (transparent)	5 (transparent)	4 (transparent)
o-Xylene	6 (transparent)	5 (transparent)	5 (transparent)
Mesitylene	5 (transparent)	4 (transparent)	4 (transparent)
1,1,2,2-Tetrachloroethane	6 (translucent)	6 (translucent)	5 (translucent)
Tetrachloroethylene	6 (transparent)	6 (transparent)	5 (transparent)
Tetralin	6 (translucent)	5 (translucent)	5 (translucent)
n-Octane	4 (translucent)	4 (translucent)	4 (translucent)
1,1,2-Trichloroethane	7 (translucent)	7 (translucent)	6 (translucent)
Cyclohexane	5 (transparent)	5 (transparent)	5 (transparent)

Fig. 1 shows the FT-IR spectra for the CCl_4 gel and the $CHCl_3$ solution of **2**. The FT-IR spectrum of the translucent CCl_4 gel of **2** is characterized by bands attributed to intermolecular hydrogen bonding, *i.e.* 3349 (νN–H of amide), 1704 (νC=O of −COOH), and 1640 cm^{-1} (νC=O of amide), whereas the isotropic solution of **2** in $CHCl_3$ affords bands at 3450 (νN–H), 1740 (νC=O of carboxylic acid), and 1660 cm^{-1} (νC=O of amide), indicative of non-hydrogen bonding stretching vibrations. The FT-IR spectrum of the KBr pellet of **2** is similar to that of the CCl_4 gel of **2,** suggesting that the pattern of hydrogen bonding in the gel is close to that in the crystal. The sharp peak near 1704 cm^{-1} is ascribed to the C=O stretching mode of CO_2H groups, characteristic of the formation of carboxylic acid dimers.[10] These results imply that in the gel the intermolecular hydrogen bonds have been formed between the neighboring molecules of **2** and thus they form a hydrogen bond network.

The TEM image of a CCl_4 gel of **2** is shown in Fig. 2. It reveals a number of fibers, juxtaposed and intertwined by several long slender aggregations with width of *ca.* 30–100 nm. The X-ray diffraction pattern (Fig. 3) of the gel cast film from the CCl_4 gel of **2** show periodical diffraction peaks, indicating

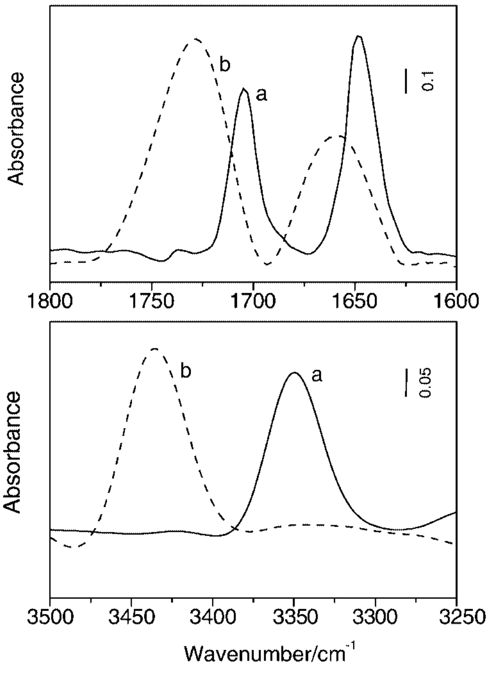


Fig. 1 FTIR spectra of **2** a) as a CCl_4 gel, b) in $CHCl_3$ solution (dashed line).

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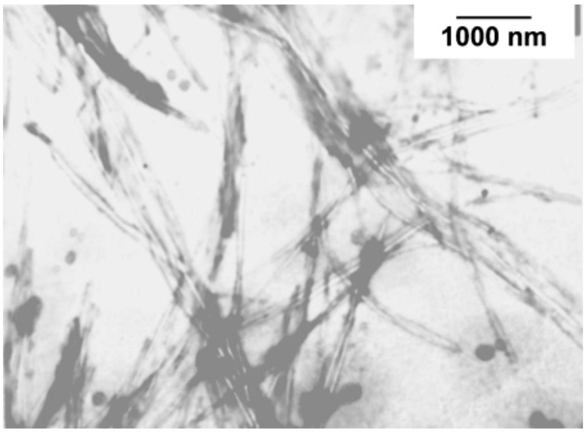

Fig. 2 TEM image of a CCl_4 gel of **2** (7 g L^{-1}). The sample was prepared by picking up the gel on a carbon grid and post-stained by uranyl acetate.

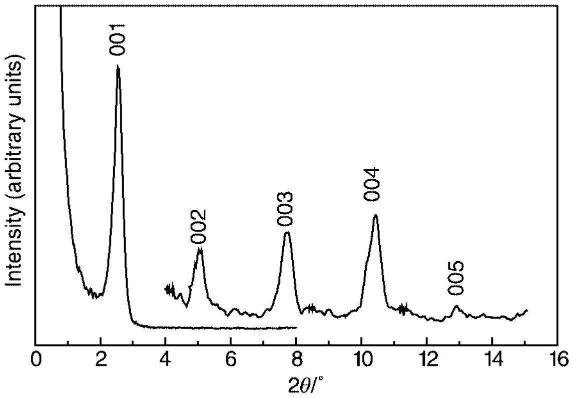

Fig. 3 X-ray diffraction patterns of a cast film from CCl_4 gel of **2**.

that **2** indeed assembles into an ordered structure. The long spacing (*D*) of the aggregate obtained by the XRD method is about 3.43 nm, which is much smaller than twice the evaluated molecular length of **2** (2.14 nm, by the CPK model), but much larger than the length of one molecule of **2**. From the XRD and FT-IR results, it can be deduced that that the gel aggregates consist of a repeating bilayer unit, which bears the head-to-head packing model with highly tilted alkyl chains relative to the bilayer normal. Within the bilayer unit, the amphiphiles are connected by intra- and inter-layer hydrogen bonds to form a hydrogen bond network and then develop the superstructure that is schematically shown in Fig. 4.

The gelling abilities of some structurally related compounds **4–8** (non-gel-forming) have been inspected. Comparing the molecular structure of **4–6** with **1–3**, it can be inferred that suitable length of the tail chain is essential for gelation since organogels fail to form when the tail chain is lengthened to 18 C atoms (**4**) or is substituted by *tert*-butoxycarbonylcarbonyl (**5**) and benzoyl (**6**). In experiment, we also find that the racemes of *N*-dodecanoylalanine do not induce any gelation, which is similar to that for *N*-dodecanoylglycine (**7**). The findings imply that the homochiral effect plays an important role in the gel formation. *N*-Dodecanoyl-L-phenylalanine (**8**), a compound containing a chiral center, does not exhibit gelling ability, which may be due to the relatively large steric hindrance effect of the benzyl group of the L-phenylalanine which weakens the intermolecular hydrogen bonding between neighboring molecules. Therefore the intermolecular hydrogen bonding is unable to meet the need for gelation. From these observations and analyses, it can be concluded that (i) gelling ability strongly depends on the L-alanine group, (ii) the hydrophile–lypophile balance is a significant factor for gelation, the suitable length of the tail chain is in the range of 8 to 14 C atoms, (iii) the formation of the bilayer aggregates and the homochiral effect play important roles in gel-forming.

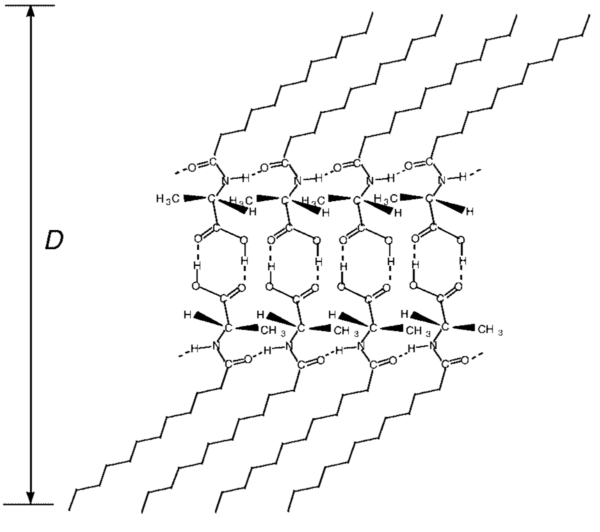

Fig. 4 Local microstructure of the bilayer aggregates of **2** in organogel.

In conclusion, this paper has shown that simple mono-chain L-alanine derivatives can self-assemble into bilayer aggregates through intermolecular hydrogen bonding and the homochiral effect in a number of organic liquids, which are juxtaposed and interlocked by van der Waals interaction, and finally gelate the organic liquids.

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Notes and references

† Amino acid (0.05 mol) is placed in a three-necked round-bottomed flask, filled with an efficient stirrer, and dissolved in 50 mL of 1 M NaOH. The flask is then almost completely immersed in a bath of ice and water (*T ca.* +3 °C) and the stirrer is now set in very rapid motion. To the solution are added, dropwise, 0.10 mol of pure acyl chloride and 80 mL of 1 M NaOH at the same rate. When the reaction is complete, the suspension is acidified carefully with 2 M HCl. The residue obtained after filtration is extracted with petroleum ether to remove the fatty acid. The final amino acid derivative is chromatographed on a silica gel column empolying appropriate solvent. Satisfactory ^1H NMR, IR, element analysis and optically activity data were obtained for the corresponding amino acid derivatives.

‡ The minimum gel concentration was calculated as described in the literature.[8] The gels were stable in a sealed tube for over two weeks. On reheating, the physical gelation is reversible.

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