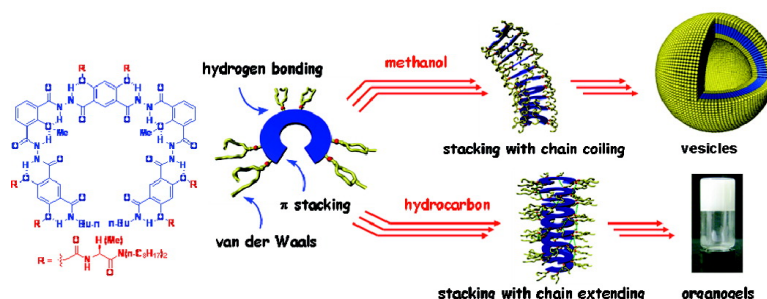


## Vesicles and Organogels from Foldamers: A Solvent-Modulated Self-Assembling Process

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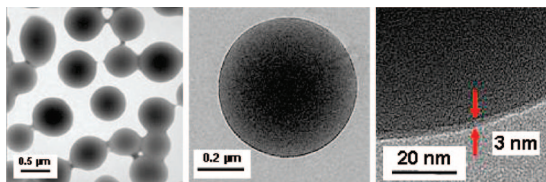
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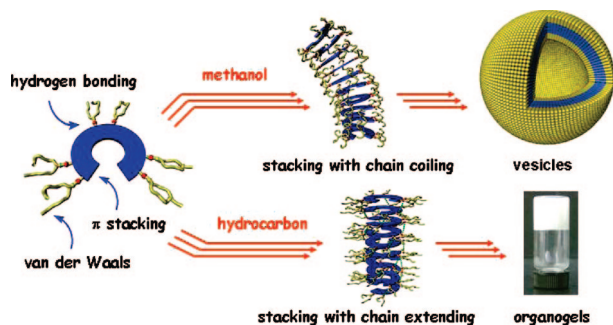
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**Figure 3.** TEM images of the vesicles of **2a** (formed in 0.25 mM solution in methanol) on copper grid covered with Formvar film at different magnifications.



**Figure 4.** Tentative model for the self-assembly of vesicles and organogels from nonamphiphilic foldamers.

1.8 nm, whereas the peripheral chains at their extended state had a length of 1.6 nm. Thus, these results showed that the vesicles had a monolayer morphology and were generated by two-dimensional packing of cylindrical aggregates of the folded frameworks (Figure 4). The more polar aryl amide groups might be exposed to methanol, while the appended alkyl chains might be repelled by solvophobic effects to entangle each other along the cylinders. It has been reported that six-membered  $N-H\cdots O$  H-bonding survives in aromatic amides in competitive media.<sup>15</sup> The NH signal of model molecule *N,N'*-di(2-methoxybenzoyl)hydrazine and its 4-substituted isomer in <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub> (4 mM) appeared at 10.75 and 10.20 ppm,<sup>13a</sup> respectively. This large difference suggested that similar H-bonding also formed in hydrazide derivatives, which could induce the formation of folded conformations for **1** and **2** in polar solvents. Similar one-layered structures have been revealed for several linear amphiphilic conjugated systems.<sup>9</sup>

Interestingly, compounds **1** and **2b** were also found to gelate nonpolar aliphatic hydrocarbons including *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, and *n*-decane. The solubility of **2a** was low in these liquids possibly due to stronger intermolecular H-bonding of its appended amides. However, both SEM and AFM studies showed that all three molecules formed entangled fibers when cast from these liquids. In contrast, only small particles and/or short fibers were formed when cast from chloroform. In nonpolar liquids,  $\pi$  stacking should exist for all these molecules. IR spectra of **1**, **2b**, and several intermediates in *n*-hexane exhibited NH stretching vibrations only at  $<3390\text{ cm}^{-1}$ , indicating that NH units in their side chains also formed intermolecular H-bonding. However, the peripheral aliphatic chains would be flexible. Therefore, we proposed that it was these flexible chains that entwined with each other, leading to the formation of three-dimensional networks which immobilized the liquid (Figure 4). Compared to those recorded in good solvent chloroform, UV spectra of the oligomers in both methanol and alkanes also exhibited hypochromicity, which increased with temperature decrease. In addition, chiral **2b** displayed circular dichroism in methanol or alkanes, which was temperature-

dependent, but not in chloroform. These results further supported  $\pi$  stacking of the oligomers.

In summary, we have shown that nonamphiphilic foldamers self-assembled to form monolayered vesicles in methanol owing to cooperative  $\pi$  stacking, hydrogen bonding, and van der Waals interactions. The fact that **1** and **2b** gelated nonpolar hydrocarbons illustrates that the self-assembly of foldamers can be modulated through appending additional groups. It is expected that both the folded segments and peripheral chains can be readily modified. Thus, the work may open the way for the design of a new generation of vesicles from nonamphiphilic architectures.

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**Supporting Information Available:** Experimental details, spectra and microscopy images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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