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FT–IR studies on Langmuir–Blodgett films of novel phosphorus amphiphiles: spontaneous polycondensation at the air/water interface

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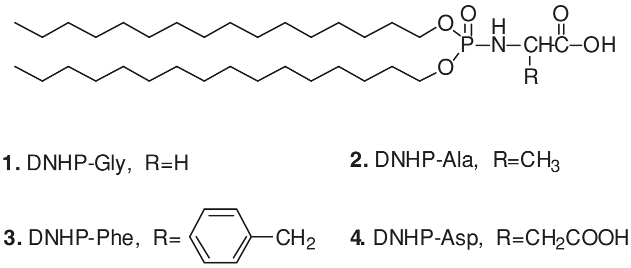
A series of amphiphilic N-(O,O-dihexadecyl)phosphorylamino acids were designed and synthesised, and the transmission FT–IR spectroscopic investigation of their Langmuir–Blodgett films (LB films) on CaF_2 substrates indicates the spontaneous polycondensation at the air/water interface before the deposition.

Keywords: air/water interface, amphiphiles, FT–IR, LB films, polycondensation

The reactions within highly ordered supramolecular systems such as Langmuir–Blodgett films (LB films) and liposomes etc. are of great interest for their outstanding rapidity and structural specificity from the arrangement of the functional groups in the molecules.[1] Since the polycondensation of amino acid based amphiphiles in LB films was first reported by Katchalsy *et al.*,[2] this research field has drawn much attention with regard to possible approaches to new materials that would be compatible between artificial materials and natural biomaterials due to the amino acid moiety.[3,4] In the prebiological sense, the LB Film of amino acid based amphiphiles could be served as an excellent model system for the self-assembly processes at the early stages of evolution in the formation of primitive biopolymers.[4,5] It has been shown in our group that N-phosphorylamino acids and peptides are chemically active species,[6] which might be related to the prebiotic synthesis of proteins and nucleotides and the phosphorylation or dephosphorylation of proteins.[7] The double-chain amphiphiles based on N-phosphorylamino acids previously synthesised are very similar in structure to lipid molecules,[8,9] the basic building blocks of all natural biological membranes. We present here evidence that four amphiphilic N-phosphorylamino acids (Scheme 1) can form stable monolayers at the air/water interface, which can be deposited successfully onto CaF_2 substrates by the well-established LB technique.[10] The transmission FT–IR spectroscopic investigation indicates that polycondensation occurs spontaneously at the air/water interface with maintenance of the supramolecular structures.



Scheme 1 Structures of N-(O,O-dihexadecyl)phosphorylam ino acids

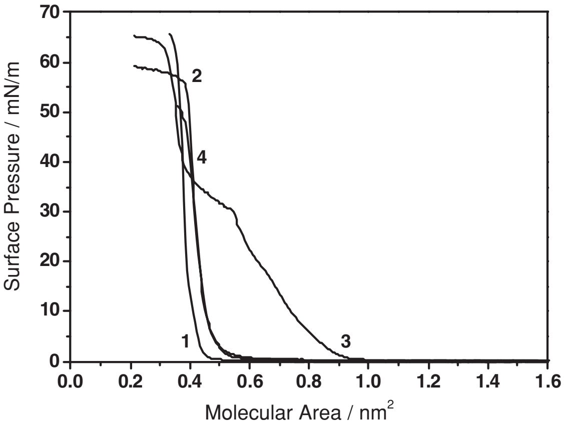


Fig. 1 π-A isotherms of N-(O,O-dihexadecyl)phophorylamino acids (*T*=20 °C).

The four amphiphiles with different amino acid moiety as head groups can form fairly stable monolayers at the air/water interface. The π-A isotherms of the four compounds are shown in Fig. 1. It is noticeable that π-A isotherms of **2** and **4** are quite similar except for the different collapse point. The linear region of a condensed film of the amphiphile is extrapolated to zero surface pressure, and the mean cross-sectional area per molecule of each N-phosphorylamino acid is obtained. The collapse point and the area per molecule of each amphiphiles are listed in Table 1. The mean molecular area of **2** is slightly larger than that of **1**, which may be the result of the geometric hindrance of the methyl of alanine. **4** has nearly the same mean molecular area as **2** since the enhanced hydrogen bond network throughout the highly polar head groups can compensate for the geometric effect of the bulky carboxyl group in the side chain of the asparic acid moiety. It is notable that the π-A isotherm of **3** exhibits a distinct phase transition region in the surface pressure range of 30–40 mN/m (Fig. 1). Taking account of the molecular dimensions of

Table 1 Monolayer properties of N-(O,O-dihexadecyl)phophorylamino acids

Amphiphiles	Collapse point (mN/m)	Area per molecule (nm^2)	Deposition pressure (mN/m)
1 DNHP-Gly	65	0.41	20
2 DNHP-L-Ala	55	0.46	25
3 DNHP-L-Phe	62	0.51[a]	40
4 DNHP-L-Asp	50	0.46	20

[a]Area per molecule in condensed phase.

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the CPK model of benzene (0.70nm×0.65nm×0.36nm), it is considered that there occurs an oriented change of the molecules,[11] that is, the phenyl rings lying flat on the water surface stand up upon the continuous compression.

The monolayers were deposited onto the CaF_2 substrates successfully at their respective optimal surface pressure by the well-established LB technique.[10] The deposition pressures for each amphiphile are also listed in Table 1. The transmission FT–IR spectra of the 33-monolayer LB films in the spectral range 1200–2000 cm^{-1} are shown in Fig. 2. The spectra of all the LB films display a distinct broad band in the spectral range 1500–1660 cm^{-1} (overlapping of the amide |and amide || band), at the expense of the decrease or disappearance of the C=O absorption at 1736 cm^{-1}, as compared with their KBr-plate IR spectra for the powder (shown in Fig. 3). Although the FT–IR spectra were recorded immediately after the deposition of the LB films, the appearance of amide band occurs in all cases, which suggested fast polycondensation at the air/water interface. The $\nu(CH_2)$ frequencies at 2918 and 2850 cm^{-1} of the 33-monolayer LB films (not shown) indicates the highly ordered all *trans* zigzag conformation of hydrocarbon chains,[12] which implies that the supramolecular structures were maintained during the polycondensation process at the air/water interface and the subsequent deposition process. The FT–IR spectra of the LB films were unchanged after exposure to air at ambient temperature for 48 h, which supported that idea that the spontaneous polycondensation occurs at the air/water interface rather than after the deposition onto the CaF_2 substrates. In the case of the 11-monolayer LB films of N-(O,O-ditetradecyl)phophorylalanine reported previously,[9] the condensation occurred after the fabrication of LB films, instead of at the air/water interface. The fast polycondensation of the amphiphiles with slightly longer hydrocarbon chains implies their greater reactive activity arose from the more favoured orientation of the functional groups in the layered structures. The strengthened hydrophobic interaction from the elongation of the hydrophobic chains enhances the order of the arrangement of the amphiphilic monomers and thus favours the orientation between the hydrophilic functional groups. Meanwhile, the enhanced interaction between the amphiphilic monomers allows the fabrication of multiplayer LB films with more monolayers, which are more stable and convenient for spectroscopic investigation. We also observed that the FT–IR spectra of solid powder and solutions in chloroform for each amphiphile remained unchanged at different time intervals under ambient conditions for a long time (over days), which suggests that the amphiphilic phosphorylamino acids are very stable in bulk phases without any polycondensation. From these results, it could be concluded that it is the particular orientation and ordered packing of the monomers within the monolayers at the air/water interface that allows the occurrence of spontaneous polycondensation.

The feasibility of alteration of the hydrophilic functional groups could provide more detailed discussion of the relativity between the condensation reactivity and the orientation and packing of the amphiphilic monomers in the layered structures. It is noted that in Fig. 2 the relevant intensity of the amide band varies distinctly with the side groups in the amino acid moiety that differ in size and polarity, which indicates that the reaction reaches equilibrium at various reaction rates for different amphiphiles. To rationalise this difference, it has been proposed that there occurs a two-dimensional lattice-controlled reaction at the air/water interface.[5] **3** retains the strongest C=O absorption among the four samples, which corresponds to the loose packing of the functional groups reacting with each other due to the steric hindrance of the phenyl rings. As to the other three samples, the oriented order of the reactive groups is enhanced by the steric preference (as in the case of **1** and **2**) or by the hydrogen bond effect of the highly polarized head groups (as in the case of **4**). Therefore, the polycondensation becomes more feasible and the equilibrium moves favourably towards the resultant peptides.

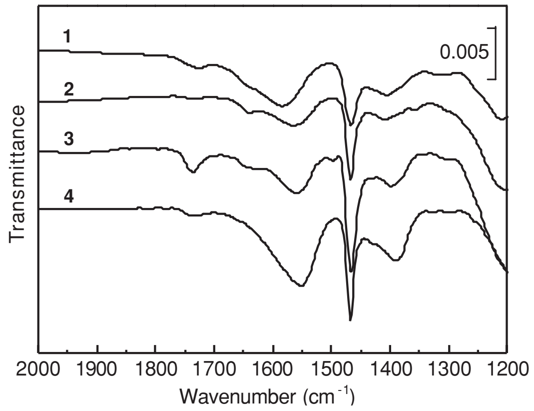

Fig. 2 Transmission FT–IR spectra of 33-monolayer LB films of N-(O,O-dihexadecyl)phosphorylamino acids (immediately after the deposition).

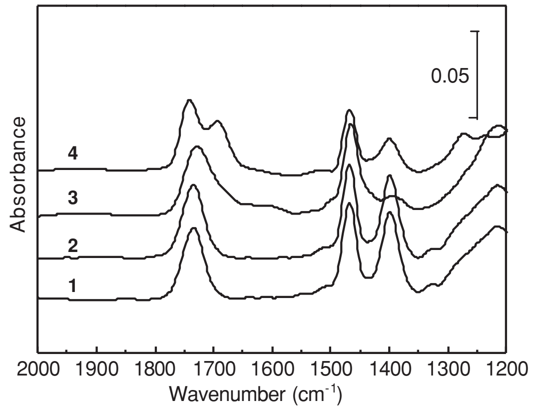

Fig. 3 KBr-plate FT–IR spectra of N-(O,O-dihexadecyl)phosphorylamino acids.

In summary, novel phosphorus amphiphiles based on amino acids were found to polycondense spontaneously at the air/water interface with the maintenance of the supramoleclar structures using the LB technique and IR characterisation. In our opinion, the research may support the theory of N-phosphorylamino acid as the co-evolution model of life origin[7] with regard to the formation of biopolymers in ordered systems being similar to the natural process occurring in cell membranes.[5, 13]

Experimental

N-(O,O-dihexadecyl)phosphorylamino acids were synthesised and purified according to the method previously reported.[8] 33-monolayer LB films were deposited from pure aqueous subphases onto CaF_2 substrates by the vertical method (dipping/lifting rate 5 mm/min) at the fixed surface pressure at 20°C with the help of a Nima 622 LB Trough. A typical time interval for deposition was around 5 h. The transmission spectroscopy was recorded on a Bruker IFS 66V spectrometer. The film spectra were obtained by subtracting the spectra of CaF_2 blank substrate from the corresponding sample spectra.

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