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Investigation of spontaneous polycondensation of N-(O, O-ditetradecyl) phosphorylalanine in highly ordered films by FTIR spectroscopy

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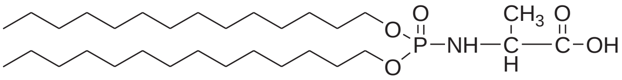
Spontaneous polycondensation to polypeptides on both cast films and Langmuir-Blodgett films (LB films) of N-(O, O-ditetradecyl)phosphorylalanine (DNTP-L-Ala) was studied by FTIR transmission spectroscopy.

Keywords: N-(O, O-ditetradecyl)phosphorylalanine, polycondensation, cast film, LB film

Currently, there is great interest in liposomes, monolayers, bilayer membranes, and Langmuir–Blodgett multilayers as biomembrane models and furthermore because of their manifold potential applicability.[1-4] Interfaces in such systems, which permit a particular arrangement of molecules, are considered to play an important role in the reactions in biological systems.[5-8] It has been shown in our laboratory that N-phosphorylamino acids and peptides are chemically active species,[9] which might be related to the prebiotic synthesis of proteins and nucleotides and the phosphorylation or dephosphorylation of proteins.[10] Long chain N-phosphorylamino acids, similar in structure to lipid molecules, the basic building blocks of all natural biological membranes, have been confirmed to form stable monolayers at the air/water interface and LB multilayers on solid substrates previously.[11] We present here an investigation by FTIR transmission spectroscopy of the spontaneous polycondensation to polypeptides on both cast films and LB films of DNTP-L-Ala (Scheme 1) deposited on CaF_2 substrates.



Scheme 1 Chemical structure of N-(O,O-ditetradecyl) phosphorylalanine (DNTP-L-Ala).

Fig.1 shows the time-dependent FTIR transmission spectra of a DNTP-L-Ala cast film on a CaF_2 substrate in the region of 2000–1300 cm^{-1}. Spectra were recorded at different time intervals after the fabrication of the film. As time advances, a broad band consisting of two peaks at 1620 and 1595 cm^{-1}, attributed to the amide I band, and the band at 1521 cm^{-1} attributed to the amide II band, emerge and increase with the decrease of the ν(C=O) band of the acid at 1732 cm^{-1}.

Fig.2 shows the time-dependent FTIR transmission spectra of an 11-monolayer LB film of DNTP-L-Ala on a CaF_2 substrate in the region of 2000–1300 cm^{-1}. Spectra were recorded at different time intervals after the deposition of the film while the zero time was set at the equilibrium point at the air/water interface. As time advances, a broad band consisting of two peaks at 1695 and 1649 cm^{-1} attributed to the amide I band and a band consisting of two peaks at 1550 and 1521 cm^{-1} attributed to the amide II band emerge and increase with the decrease of the ν(C=O) band of the acid at 1741 cm^{-1}. The similar results in both cases indicate that the acids were converted to polypeptides, which implies that polycondensation can proceed spontaneously on these ordered films without any catalyst or initiator.

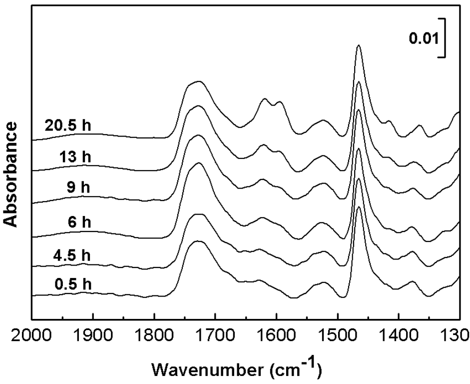


Fig. 1 Time-dependent FTIR transmission spectra of a DNTP-L-Ala cast film on a CaF_2 substrate.

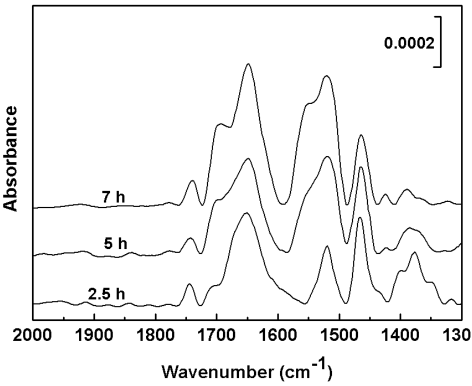


Fig. 2 Time-dependent FTIR transmission spectra of an 11-monolayer LB film of DNTP-L-Ala on a CaF_2 substrate.

There is an empirical correlation between the frequency of the amide I and amide II absorption of a protein or peptide and its predominant secondary structure.[12,13] The spectra shown in Fig. 1 exhibit the increasing amide I absorptions at 1620 and 1595 cm^{-1}, which are indicative of a predominant secondary structure of the β-sheet type in the resultant polypeptides. The amide I absorption at 1649 cm^{-1} and the amide II absorption at 1521 cm^{-1} in Fig. 2 indicate the predominance of a secondary structure of the α-helix type in LB film. It is also noted that the increase in intensity of the amide band is concomitant with the appearance of the shoulder peaks by the high wavenumber side, the frequencies of which imply the coexistence of oligopeptides with secondary structure of the β-sheet type. It has been assumed that certain interlayer and/or intralayer interactions within the highly ordered films affect the secondary structure of the resultant polypeptides, about which further work is going on.

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Experimental

DNTP-L-Ala was synthesised and purified according to the method previously reported.[14] Cast films were fabricated by casting a chloroform solution of DNTP-L-Ala on CaF_2 substrates. 11-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 32 mN/m at 20°C with the help of a Nima 622 LB Trough. FTIR transmission spectroscopy was performed on a Bruker IFS 66V spectrometer. The film spectra were obtained by subtracting the spectra of CaF_2 blank substrates from the corresponding sample spectra.

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