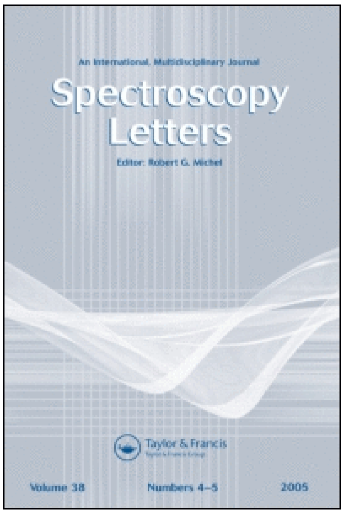

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Fourier Transform Infrared Spectroscopic Investigation on Langmuir-Blodgett Films of Octadecanoyl Ester of 1-(2-Carboxyethyl) Thymine: Molecular Orientation, Molecular Recognition to Complementary Base of Nucleic Acid and Order-Disorder Transition

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FOURIER TRANSFORM INFRARED SPECTROSCOPIC INVESTIGATION ON LANGMUIR-BLODGETT FILMS OF OCTADECANOYL ESTER OF 1-(2-CARBOXYETHYL) THYMINE: MOLECULAR ORIENTATION, MOLECULAR RECOGNITION TO COMPLEMENTARY BASE OF NUCLEIC ACID AND ORDER-DISORDER TRANSITION

KEY WORDS: Nucleolipid amphiphile, Langmuir-Blodgett film, Fourier transform infrared spectroscopy, Molecular orientation, Molecular recognition, Order-disorder transition

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ABSTRACT

Fourier transform infrared (FTIR) transmission, polarized transmission, reflection absorption (RA) and Attenuated total reflection

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(ATR) spectroscopy were employed to investigate the molecular orientation and molecular recognition to the complementary base at the air / water interface of a novel nucleolipid amphiphile, octadecanoyl ester of 1-(2-carboxyethyl) thymine. It has been found that the molecules are biaxially oriented and the hydrocarbon chain titled considerably from the substrate normal as well as the chromophoric part in the LB film. Molecular recognition through complementary bases pairing takes place at the air / water interface between the thymine moiety in the head group of the amphiphile and adenosine in the subphase, the hydrogen involved in the host-guest interactions has been detected by using FTIR-ATR technique. FTIR transmission spectra measured at elevated temperatures revealed that the order-disorder transition of the LB film which contains the complementary base occurs at lower temperature. To our best knowledge, investigation of the order-disorder transitions in nucleolipid amphiphile LB films and comparative studies of the order-disorder transitions between nucleolipid amphiphile LB film that contains and does not contain the complementary bases have been virtually nonexistent, so far.

INTRODUCTION

Organized molecular monolayers assembled by LB technique provide unique environments for molecular interactions and consequently for molecular recognition.[1, 2] The use of multiple hydrogen bonding as a means of specific recognition are currently very important due to its analogy to molecular recognition in the biological system. The mutual recognition of complementary bases in nucleic acids is known to proceed spontaneously and with high selectivity, which has been proved to be one of the most efficient mechanisms of accumulating, storing, reproducing and evolving genetic information. Surface monolayers formed by nucleic base-containing lipids provide a convenient molecular system to simulate the molecular recognition process by way of multiple hydrogen bonding that occurring at surfaces of biological molecular system.[3-6] The supramolecular system which formed by nucleolipid amphiphiles and the complementary bases should be important both in understanding molecular interactions on biological cell surfaces and in applications, such as biosensors.[7-9]

One of the important factors of LB film is its thermostability, the order-disorder transitions of molecules in LB films have been a matter of keen interest recently.[10-15] LB monolayers may be an example of a system exhibiting two-dimensional phase transitions and melting, the phase transition temperature (Tc) of which is decided by the structure of the molecules that form it. The molecular recognition in the LB films would alter the aggregation state of the molecules, which results in the change of the phase transition temperature.

Fourier transform infrared (FTIR) spectroscopy has been proved to be a powerful nondestructive structural probe for LB films.[16-18] Combination of infrared transmission and reflection absorption (RA) spectroscopy provides information about the orientation of the hydrocarbon chain and the chromphore; and the orientation of the axes of the crystal lattice can be investigated by infrared polarized spectra. The infrared features which obtained from FTIR spectra that measured at elevated temperatures can offer insight into the order-disorder transition of LB films. The FTIR attenuated total reflection (ATR) spectroscopy is considered to be an excellent tool for studying ultrathin organic films because of its high sensitivity.[19-21]

In the present study, the molecular orientation and molecular recognition capabilities at the air / water interface of a novel nucleolipid amphiphile, octadecanoyl ester of 1-(2-carboxyethyl) thymine [22] (Fig. 1), were investigated by using FTIR transmission, RA and ATR spectra. In this study, it is found that the molecules are biaxially oriented at the air / water interface. The molecular recognition between the thymine moiety in the head group of the nucleolipid amphiphile and adenosine in the subphase takes place through multiple hydrogen bonding, which leads to the increase of the orientation angle of the amphiphile molecules and looses the molecule aggregation in the LB film. These conclusions are consistent with the results that get from FTIR transmission spectra measured at elevated temperatures which indicate that the phase transition temperature would lower when the molecular recognition occurs.

EXPERIMENTAL SECTION

1. Sample Preparation:

The synthesis of octadecanoyl ester of 1-(2-carboxyethyl) thymine was reported elsewhere.[22] A computer-controlled WM-1 LB trough system with a Wilhelmy balance was employed for LB film fabrications. Several drops of octadecanoyl ester of 1-(2-carboxyethyl) thymine in chloroform ($1.0\times10^{-3}M$) were placed onto an aqueous subphase of water

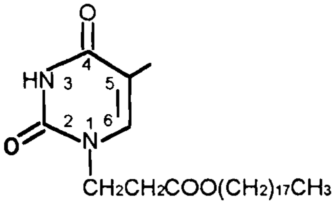

Fig. 1. Molecular structure of octadecanoyl ester of 1-(2-carboxyethyl) thymine.

which was doubly distilled from deionized water. After evaporation of the solvent, the monolayers were compressed at a constant rate of 25 cm^2/min up to the surface pressure of 30 mN/m. The π-A isotherms (Fig. 2) revealed that the spread monolayers were solid condensed films at this surface pressure no matter the subphase was pure water or 5*mM* adenosine aqueous solution. After 30 min was spent to establish an equilibrium of the monolayers, the monolayers were then transferred by the vertical dipping method onto calcium fluoride (CaF_2) plates (for FTIR transmission measurements), germanium RA plates (for FTIR RA measurements) and germanium ATR plates (for FTIR ATR measurements) at this surface pressure. All of the substrates had been cleaned successively with chloroform, acetone and ethanol and finally subjected to supersonic treatment for 30 min before use. The upstroke and downstroke motions are both 2 mm/min. The transfer ratio was found to be nearly unity (1.0±0.1) for both upstroke and downstroke when the subphase was pure water, this sort of LB film has the Y-type structure.[2] When the subphase was 5*mM* adenosine aqueous solution, there was no transfer in the downstroke mode, the transfer ratio

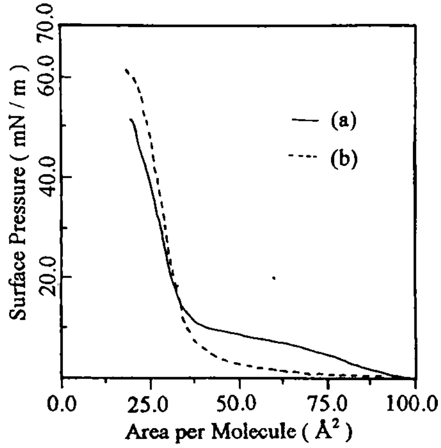

Fig. 2. Surface pressure–area (π–A) isotherms of octadecanoyl ester of 1-(2-carboxyethyl) thymine: (a) on pure water; (b) on 5*mM* adenosine aqueous solution.

decreased from nearly 1.0 in the first dipping cycle to about 0.5 in the fifth cycle, this sort of LB film has the Z-type structure.[4]

2. FTIR Measurements:

Infrared spectra were measured on a Bruker IFS 66V vacuum-type Fourier transform infrared spectrophotometer equipped with a room-temperature deuterated triglycine sulfate (DTGS) detector. The FTIR-RA spectra were obtained by using a reflection attachment of the spectrophotometer at the incident angle of 80°. A variable angle ATR attachment was used for ATR measurements. The angle of incidence was 45° and the number of internal reflections was 25. Polarized spectra were obtained with the aid of a ZnSe wire grid polarizer (Spectra-Tech. Inc.).

Atmospheric carbondioxide and water vapor were removed by using a rotary vane vacuum pump to evacuate both the sample chamber and the optics chamber of the spectrophotometer while the spectra were measured. One thousand interferograms were coadded at a resolution of $4cm^{-1}$ to achieve good signal-to-noise ratios of the spectra. All spectra here were results of subtraction of the curves measured with the clean substrates from those measured after transferring the respective films on the same substrate. In order to measure the infrared spectra at elevated temperatures, the CaF_2 plates on which the LB film had been deposited was inserted into a sample holder with heaters. Temperature control was achieved by using a P/N 21.500 automatic temperature controller (Graseby specac Inc.). After raising the temperature to the preset value and keeping it within ±1°C for 15 min, the FTIR transmission spectra measurements started. The bandwidths of CH_2 symmetric stretching were determined by computing the width at one-half of the peak heights. The band area were gained by a computer system for infrared measurements and analyses on the spectrophotometer. The temperature-induced changes in infrared frequencies and bandwidths were both reproducible.

RESULTS AND DISCUSSION

1. Molecular Orientation of Octadecanoyl Ester of 1-(2-Carboxyethyl) Thymine at the Air / Water Interface:

Fig.3 exhibits FTIR transmission spectra of the 1-, 3-, 5-, 7-, 9-monolayer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine dropped from pure water. All the spectra were very similar to each other except the band intensities. It can been seen from the spectra that the

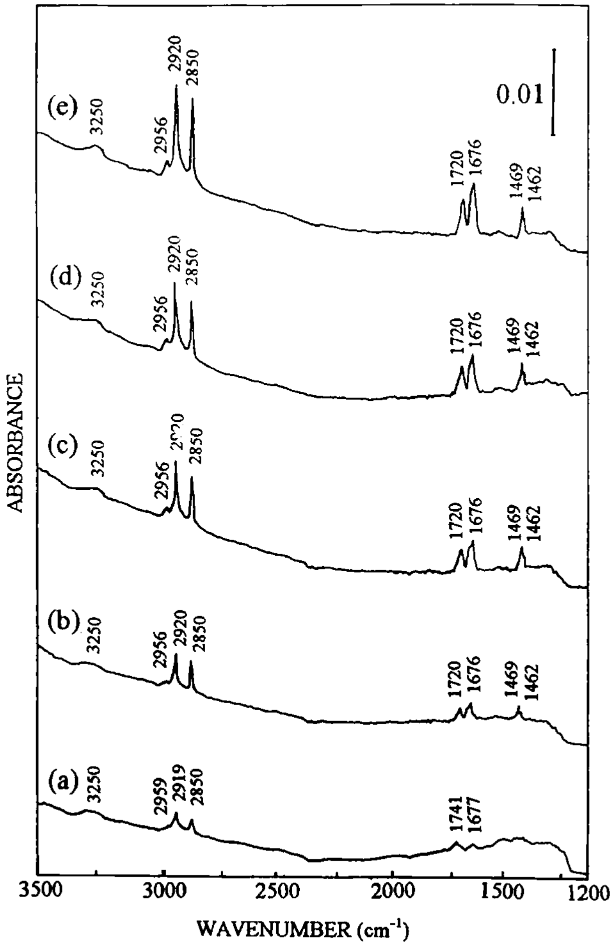

Fig. 3. FTIR transmission spectra of (a) 1-, (b) 3-, (c) 5-, (d) 7-, (e) 9-monolyer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited on CaF_2 substrates from pure water.

band intensities increased almost linearly with increasing number of monolayers, *n* (Fig. 4), which suggesting that the conformation, subcell packing, and molecular orientation of octadecanoyl ester of 1-(2-carboxyethyl) thymine in the LB films change little as a function of *n* value. As for the spectra of 1-monolayer, the band broadening effect in the region of 1800–1200cm^{-1} is due to the strongly ionic nature of CaF_2 substrate, which must induce particular interactions between the monolayer polar heads and the substrate. In Fig. 3, bands at 3250, 2956, 2920 and 2850cm^{-1} are attributed to the NH stretching mode, CH_3 symmetric stretching mode, CH_2 antisymmetric and symmetric stretching mode of the hydrocarbon chain, respectively. The frequencies of the CH_2 antisymmetric and symmetric stretching bands are very sensitive to the conformation of the hydrocarbon chain. When the alkyl chains are highly ordered (*trans-zigzag* conformation), the bands appear near 2918 and 2850cm^{-1}, respectively. While the upward shifts of the bands are indicative of the increase in conformation disorder, that is to say, *gauche* conformers, in the hydrocarbon chains.[23, 24] Thus the conclusion can be reached that the LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine have highly ordered hydrocarbon chains. In Fig. 3, the band near 1720cm^{-1} was due to C=O (2) (Fig. 1) stretching mode, while the band near 1676cm^{-1} was assigned to an overlap of C=O (4) stretching mode, C=C stretching mode and C=O (ester) stretching mode. Because the CH_2 scissoring band of the hydrocarbon chains is sensitive to the intermolecular interactions, the molecular subcell packing in the LB films can be deduced from it.[25-27] The doublet near 1456cm^{-1} in Fig. 3 indicates

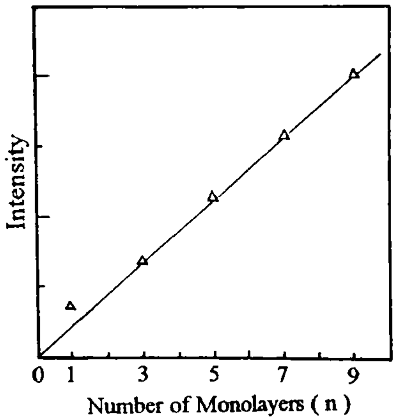

Fig. 4. Intensity of the CH_2 symmetric stretching band plotted against the number of monolayers (*n*).

that the hydrocarbon chains of octadecanoyl ester of 1-(2-carboxyethyl) thymine in the LB films are in orthorhombic subcell packing.

Fig. 5 (a) and (b) show the polarized infrared transmission spectra of the 5-monolayer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited on CaF_2 plates from pure water and 5*mM* adenosine aqueous solution, respectively. These spectra were measured by using polarized infrared light with the electric vectors perpendicular and parallel to the direction of dipping. A moderate dichroism $A_{\perp}/A_{//}=1.10$ was observed for the CH_2 symmetric stretching vibration mode for the 5-monolayer LB film dropped from pure water; as for the 5-monolayer LB film dropped from 5*mM* adenosine aqueous solution, the dichroic ratio was found to be 1.27. This deviation from unity implies that the octadecanoyl ester of 1-(2-carboxyethyl) thymine molecules in the LB

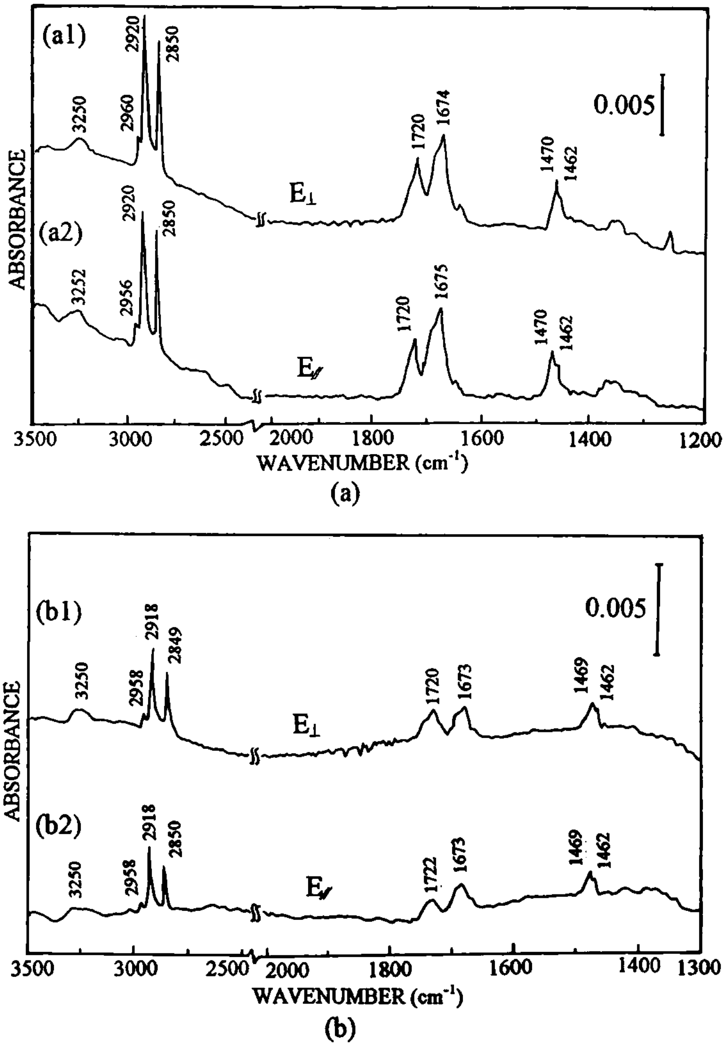

Fig. 5. Polarized FTIR transmission spectra of 5-monolayer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine: (a) deposited from pure water; (b) deposited from 5*mM* adenosine aqueous solution. The electric vectors of the polarized infrared light were perpendicular (a1, b1) and parallel (a2, b2) to the dipping direction, respectively.

films have some preferential orientation along the dipping direction, that is to say, they are biaxially oriented.[28] The molecules in the LB film that transferred from 5*mM* adenosine aqueous solution oriented along the dipping direction more distinctly.

Fig. 6 (a) and (b) exhibit the FTIR transmission and RA spectra of 5-monolyer LB film of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited from pure water and 5*mM* adenosine aqueous solution, respectively. In FTIR transmission measurements, the electric field of the infrared beam is parallel to the film surface, while in FTIR-RA measurements is mainly perpendicular. According to the surface selection rule in infrared RA spectroscopy, vibrational modes with their transition moments perpendicular to the substrate surface are enhanced in a RA spectrum.[29-32] It can be seen from Fig. 6 (a) that the CH_2 antisymmetric and symmetric stretching bands both have medium intensities in infrared transmission and RA spectra, which indicates that the hydrocarbon chains in the LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine are neither parallel nor perpendicular to the substrate surface, but being titled considerably from the surface normal.[33] In the RA spectrum of LB film transferred from pure water (Fig. 6 (a2)), the band near $1284cm^{-1}$ was assigned to an overlap of ring stretching vibration and CH in-plane bending vibration. The band near $1456cm^{-1}$ was ascribed to a coupled mode of the CH_2 scissoring and the asymmetric bending of the terminal methyl group, which is believed to have resulant dipole displacement perpendicular to the $C{-}CH_3$ bond of the hydrocarbon chain. The enhancement of this band in the RA spectrum compared with that in

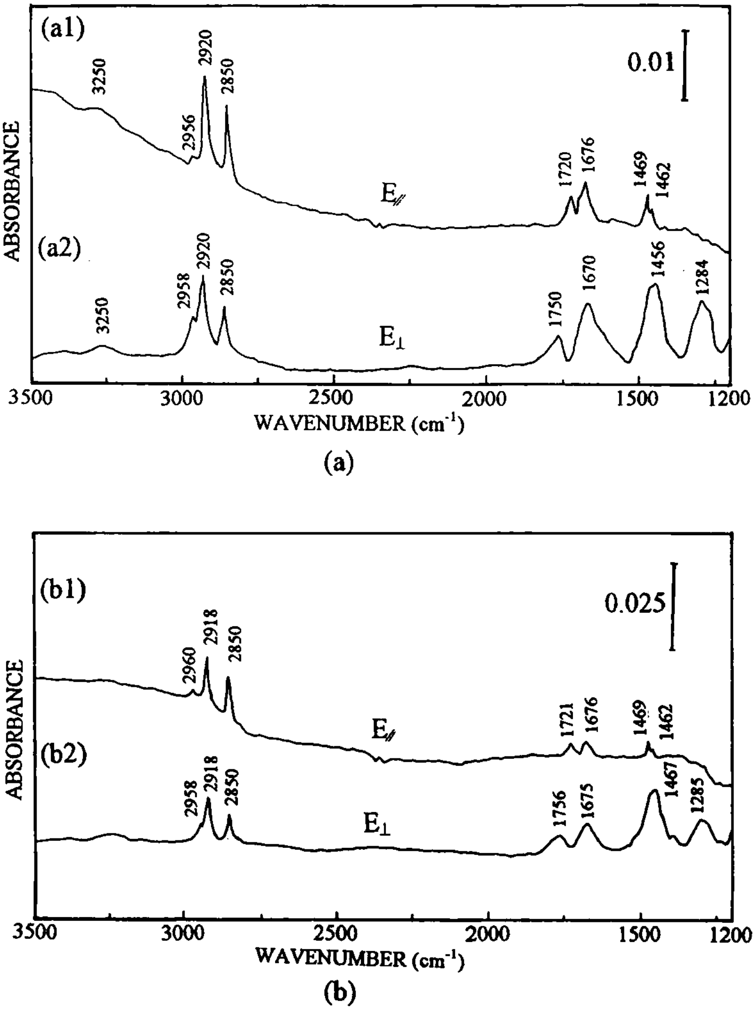

Fig. 6. FTIR transmission (al, bl) and RA (a2, b2) spectra of 5-monolyer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine transferred from pure water (a) and 5*mM* adenosine aqueous solution (b), respectively.

the transmission spectrum suggested that the hydrocarbon chain took slantingly oriented states in the LB film. The intensities of the in-plane vibrating mode, such as C=O stretching mode, also increased in the RA spectrum, which indicating that the thymine plane titled considerably from the surface normal in the LB film. As for the LB film deposited from 5*mM* adenosine aqueous solution, analogous conclusions can be obtained (Fig. 6 (b)).

2. Molecular Recognition of Octadecanoyl Ester of 1-(2-Carboxyethyl) Thymine to Adenosine at the Air / Water Interface:

From the FTIR transmission spectra of the LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine transferred from 5*mM* adenosine aqueous solution, no additional characteristic IR peaks of adenosine could be found as compared with that transferred from pure water. This may be due to the lower transfer ratio when transferring LB films from 5*mM* adenosine aqueous solution compared to that from pure water, which could be explained by the thymine-adenosine interaction. Secondarily, the molar ratio of nucleolipid amphiphiles to the complementary bases is rather low in the molecular recognition system fabricated in LB films.[19, 34] Furthermore, the sensitivity of the infrared transmission method is rather insufficient. In infrared transmission measurements, only the vibrational modes with their transition moments parallel to the substrate surface can be observed, then if the chromophores in the LB film titled from the surface normal, it would be hard to be detected. So, FTIR-ATR techniques was employed to investigate the molecular recognition of octadecanoyl ester of 1-(2-carboxyethyl) thymine to adenosine at the air / water interface. In FTIR-ATR measurements, the angle of the electric field of the infrared beam and the normal of the substrate is 45°, so if the chromophores in the LB films oriented titled from the surface normal, it can be detected easily. Fig. 7 (a) and (b) show the FTIR-ATR spectra of 9-monolyer and 5-monolayer LB films transferred from pure water and 5*mM* adenosine aqueous solution, respectively. A great difference can be observed from the two spectra. In Fig. 7 (a), characteristic vibration modes of thymine group are shown: 3248cm^{-1} (NH stretching), 1720cm^{-1} (C=O (2) stretching), 1676cm^{-1} (overlap of C=O (4) stretching, C=C stretching and C=O stretching (ester)), 1646cm^{-1} (ring stretching). Some characteristic vibrating bands of adenosine which induced into the LB film by molecular recognition action could be observed in Fig. 7 (b): 1685cm^{-1} (NH_2 scissoring), 1602cm^{-1} (ring stretching) and 1543cm^{-1} (overlap of NH_2 scissoring and ring stretching).[35] The band near 1646cm^{-1} increased its intensity markedly between Fig. 7 (a) and (b), this may be due to an overlap of the ring stretching and bonded NH_2 scissoring (adenosine). In the high frequency region, compared to Fig. 7 (a), the band near 3248cm^{-1} broadened in Fig. 7 (b) in addition to two new peaks near 3335cm^{-1} and 3257cm^{-1} which attributed to NH stretching mode of adenosine can be found. These spectral features can be explained as a result of the formation of the complementary multiple hydrogen bonds between thymine group and adenosine, a schematic drawing of which is shown in Fig. 7. Because of the formation of the complementary multiple

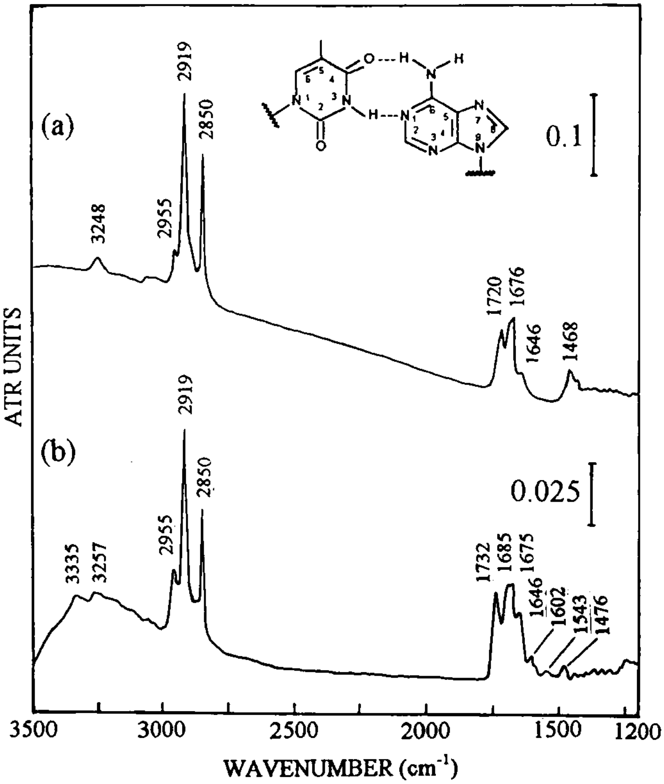

Fig. 7. FTIR-ATR spectra of LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine: (a) 9-monolyer transferred from pure water; (b) 5-monolyer transferred from 5*mM* adenosine aqueous solution.

hydrogen bonds, a shift of the C=O (2) (thymine group) stretching mode from 1720cm^{-1} to 1732cm^{-1} could be found. The band of CH_2 scissoring mode decreased its intensity and shift upward from 1468cm^{-1} to 1476cm^{-1} , which means the orientation of the hydrocarbon chains are different from each other under the two conditions. The hydrocarbon chains that in the LB films transferred from 5*mM* adenosine aqueous solution oriented slanter than those from pure water, the packing density of the molecules in the LB film also decreased. The band progress in the region between 1400cm^{-1} and 1200cm^{-1} in Fig. 7 is due to the CH_2 wagging vibrations of the *trans-zigzag* hydrocarbon chains,[20] which agrees well with the conformation characters of the hydrocarbon chains that demonstrated from the CH_2 stretching bands observed in Fig. 3.

3. Order-disorder Transition of LB Films of Octadecanoyl Ester of 1-(2-Carboxyethyl) Thymine:

Temperature-induced spectral changes observed for 9-monolayer and 5-monolayer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited on CaF_2 plates from pure water and 5*mM* adenosine aqueous solution are shown in Fig. 8 and Fig. 9, respectively. The frequencies and bandwidths of CH_2 antisymmetric and symmetric stretching bands are sensitive to the conformation and mobility of the hydrocarbon chains, respectively; while the alteration in the band areas of the bands results partly from a change in chain packing density and partly from a change in the orientation of the hydrocarbon chains.[36] It can be seen from Fig. 8 and Fig. 9 that for both of these two sorts of LB films, the bandwidths and band areas of the CH_2 stretching mode change in parallel with their frequencies, suggesting that the mobility of the hydrocarbon chains increases with the progress of disordering. Fig. 10 illustrates temperature dependence of the frequency, bandwidth, and band area of CH_2 symmetric band for the two sorts of LB films. For the LB film transferred from pure water, the antisymmetric and symmetric

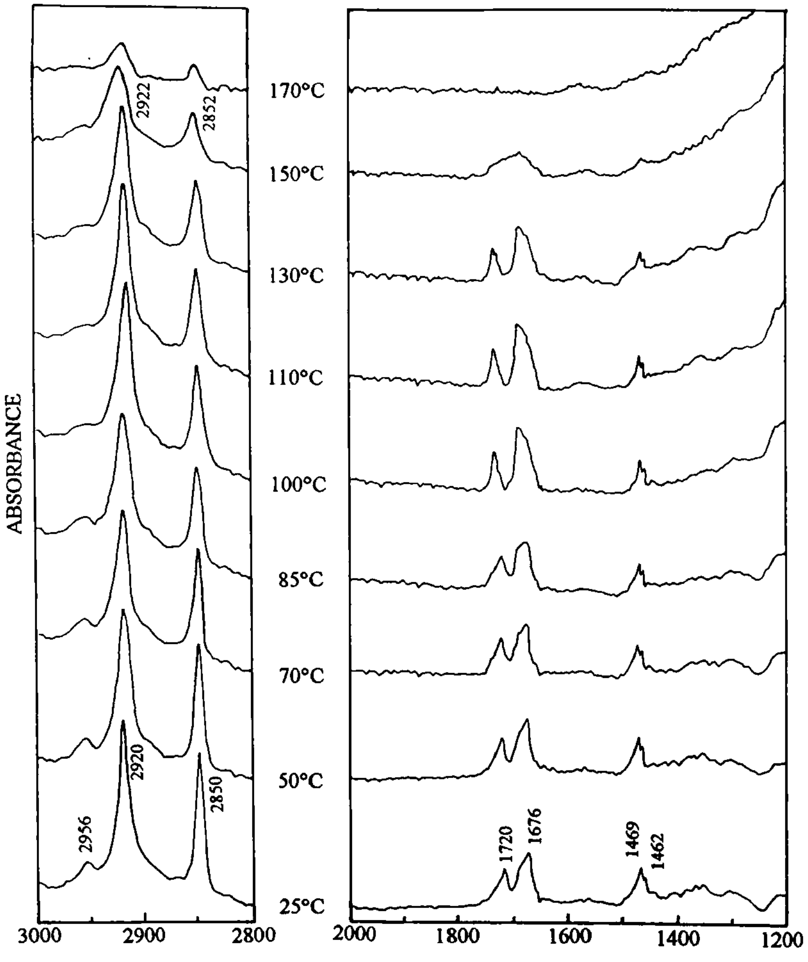

Fig. 8. FTIR transmission spectra of 9-monolayer LB film of octadecanoyl ester of 1-(2-carboxyethyl) thymine transferred from pure water at elevated temperatures.

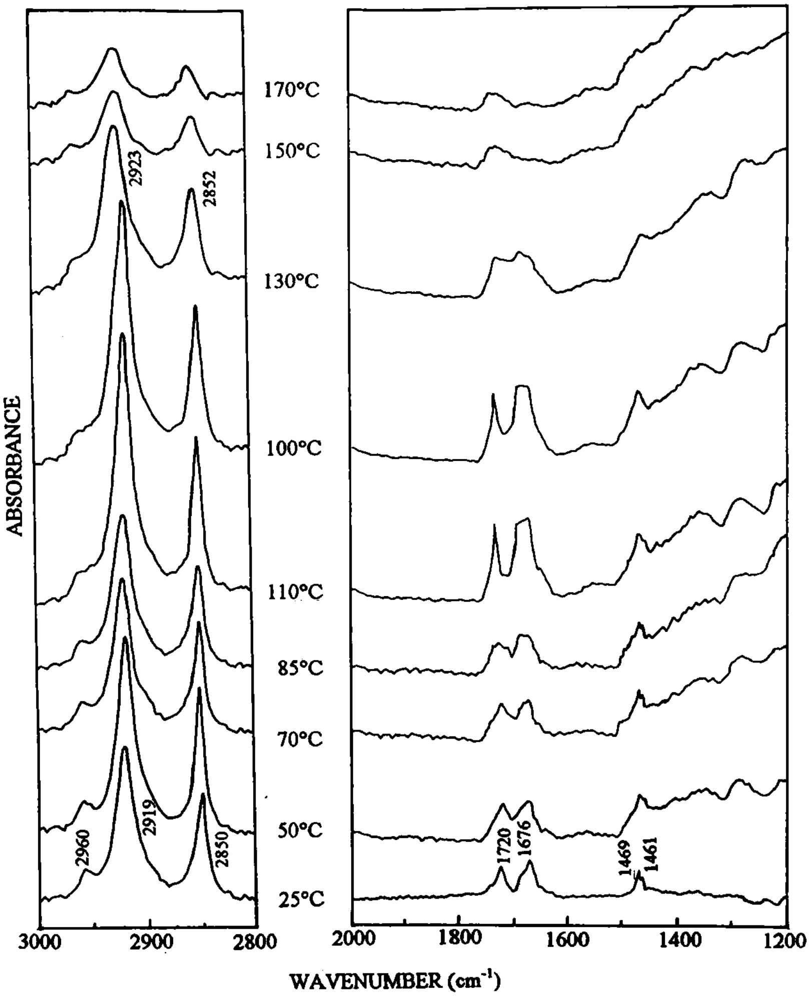

Fig. 9. FTIR transmission spectra of 5-monolayer LB film of octadecanoyl ester of 1-(2-carboxyethyl) thymine transferred from 5*mM* adenosine aqueous solution at elevated temperatures.

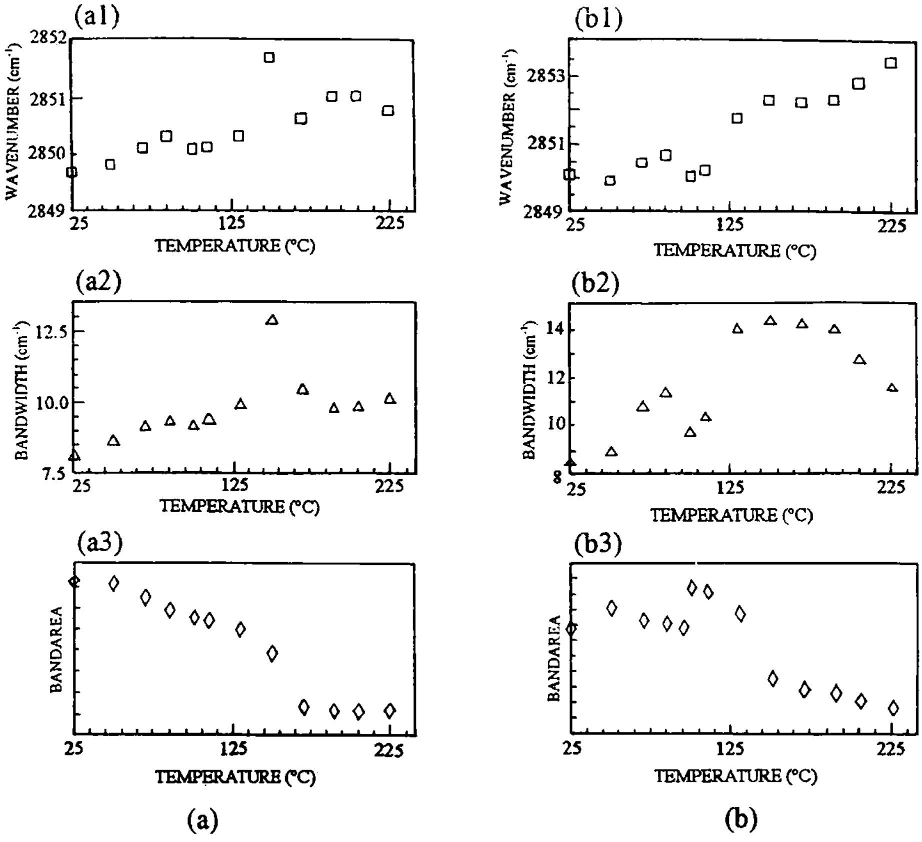

Fig. 10. Temperature dependence of the frequency, bandwidth and band area of the CH_2 symmetric stretching band of the 9-monolayer and 5-monolyer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited on CaF_2 plates from pure water (a) and 5*mM* adenosine aqueous solution (b), respectively.

bands of CH_2 show an abrupt upward shift to 2922cm^{-1} and 2852cm^{-1} in the temperature region of 130–150°C, respectively. And the bandwidths increase, the band intensities decrease simultaneously in the temperature region. It can be concluded from all of the spectral features that the molecule aggregation in the LB film transferred from gel state into liquid crystalline phase. In the low-frequency region, the bands of carbonyl shifted upward, the CH_2 scissoring band gradually decreased and finally vanished in the process of being heated. As for the LB film transferred from 5*mM* adenosine aqueous solution, the frequencies, bandwidths and band areas of CH_2 antisymmetric and symmetric stretching bands showed their abrupt changes in the temperature region of 110–130°C. The bands of carbonyl shifted to high wavenumber and the band intensities increased drastically at about 110°C. The CH_2 scissoring band also decreased gradually and disappeared ultimately. The intensity ratio of the symmetric and antisymmetric CH_2 stretching mode ($I\nu_s(CH_2)/I\nu_a(CH_2)$) can be used as an indicator to discuss the molecular orientation of the alkyl chain in LB films.[37] For the LB film transferred from pure water, the values of $I\nu_s(CH_2)/I\nu_a(CH_2)$ do not change much till 70°C (Fig. 11 (a)); while for that transferred from 5*mM* adenosine aqueous solution, the values of $I\nu_s(CH_2)/I\nu_a(CH_2)$ decrease straightly in the process of being heated (Fig. 11 (b)). That is to say, in the latter sort of LB film, the reorientation of the hydrocarbon chains occurs at lower temperature in the process of phasetransition. The distinction between the phasetransition of the two sorts of LB films is due to the existence of adenosine which introduced into the LB film by the complementary

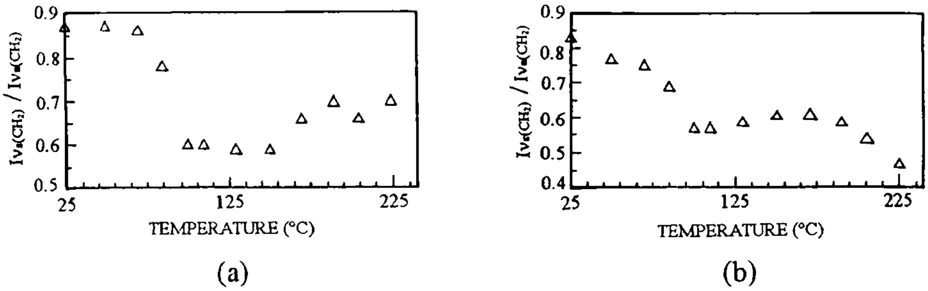

Fig. 11. Temperature dependence of $Iv_s(CH_2)/Iv_a(CH_2)$ of the 9-monolyer and 5-monolyer LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine deposited on CaF_2 plates from pure water (a) and 5*mM* adenosine aqueous solution (b), respectively.

multiple hydrogen bonds. When the molecular recognition effect between the thymine groups and the adenosine molecules occurs in the LB film, the orientation angle of the hydrocarbon chains would increase, the mobility of the alkyl chains would raise and the chain packing density would decrease. So the order-disorder transition of this sort of LB film can occur under comparatively moderate condition.

CONCLUSIONS

Conclusions obtained in the present study have revealed the following:

(a). In the LB films of octadecanoyl ester of 1-(2-carboxyethyl) thymine, the molecules are biaxially oriented, both the hydrocarbon chain and the chromophore titled considerably from the substrate normal. The molecular recognition effect with adenosine would increase the orientation angle.

(b). Molecular recognition between the thymine groups of the nucleolipid amphiphile and the adenosine molecules takes place at the air / water interface through the complementary multiple hydrogen bonds.

(c). The molecular recognition between complementary bases would result in the drop of the phasetransition temperature of the LB film that formed by nucleolipid amphiphiles.

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