

Molecular Arrangement and Recognition of a New Bolaform Cinnamic Acid Derivative in LB Films*

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Abstract A bolaamphiphile containing cinnamic acid moiety, [4-(10-hydroxydecanyloxy)-10-hydroxydecanyl-cinnamate, abbreviated HDC], was synthesized and the LB films of HDC were studied. It was found from the results of π -A isotherms that multilayers of HDC were formed at the air/water interface. The photoreaction of HDC in LB films induced by UV light was investigated with UV and IR measurements. Photodimerization also took place in the mixed LB films of HDC and 1,16-hexadecanediol. The spectra results showed that the HDC molecules assembled orderly due to the separated recognition of π - π interaction and the zigzag stacking of methylene groups. XRD studies indicated that bilayers formed in the LB films with a tilt angle of 58.8° and 53.2° before and after UV irradiation, respectively. A packing model of HDC was also proposed.

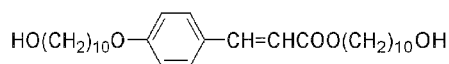
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Researches on the bolaamphiphiles (molecules with two polar headgroups connected by one or two hydrocarbon chains) are attracting much interests^[1-5] since they can provide monolayer membranes. Most of researches on bolaamphiphiles are concerned with the aggregation behaviors in aqueous solution^[6-9]. Little work has shed light on the LB films formed by bolaamphiphiles^[10]. Different from conventional amphiphiles, upright conformation, most bolaamphiphiles bend at the air/water interface with their two headgroups contacting water^[11-14]. Thus the conformation of bolaamphiphiles in LB films is not unique as that of conventional amphiphiles due to the special molecular structure of bolaamphiphiles. Both the two polar headgroups can attach to the substrate. Therefore, the research on the molecular conformation in LB films of some typical bolaamphiphiles will be of great importance for understanding the molecular interaction and recognition mechanism. Considering the advantage of cinnamic acid derivatives in the research of molecular assemblies^[15-18], the study of the photodimerization of bolaform cinnamic acid derivatives in LB films can provide detailed information of molecular arrangement. It is well known that the LB films can provide a readily controllable and ordered environment in which molecules are restricted in their balance positions^[18-19], so the

research on the dimerization of cinnamic derivatives in LB films can provide detailed insight into the molecular arrangement and recognition. Since Schmidt^[20] firstly found that solid state cinnamic acid and its derivatives underwent photodimerization upon UV irradiation, similar photodimerization processes in the LB films have been the subjects of many groups^[21-22]. However, most of these works focus on the conventional amphiphiles of cinnamic acid derivatives, in which molecules definitely assembled in LB films with their polar head groups rooting in the substrate^[18,22]. Thus the group recognition, such as the π - π interaction, in LB films can not be fully studied due to the restriction of the surfactant molecular conformation.

In this paper, we firstly incorporated the cinnamyl group into a bolaamphiphile 4-(10-hydroxydecanyloxy)-10-hydroxydecanyl-cinnamate (abbreviated as HDC, Scheme 1), and investigated the photodimerization behavior of HDC both at the air/water interface and in its LB films to obtain the information about the molecular configuration and interaction among HDC molecules. It is interesting to find that the HDC molecules formed multilayers at the air/water interface and built up tilt bilayers in the LB films. In addition, the molecules showed high group recognition ability which is attributed to the co-contribution of π - π interaction

and zigzag packing of methylene group among HDC molecules. This is the first report about the conformation of bolaamphiphiles in LB films. The simple but strong group recognition was also observed in HDC and its mixed LB films with 1,6-hexadecanediol.



Scheme 1 Structure of HDC

1 Experiments

1.1 Synthesis of HDC

HDC was synthesized according to the following procedure: firstly, 1-bromo-10-hydroxydecane was prepared from the corresponding diol and hydrobromic acid^[23] (Beijing Chemical Co., A.R.). Then a mixture of 4-hydroxy cinnamic acid (Sigma Co., 1.64 g, 0.01 mol), 1-bromo-10-hydroxydecane (2.40 g, 0.01 mol) and 7 mL potassium hydroxide (1.12 g, 0.02 mol) aqueous solution in 100 mL of acetone was refluxed for 72 h. The reaction mixture was poured into a large amount of distilled water after acidification with 3 mol·L⁻¹ HCl. White solid was obtained after the solution being cooled. The solid was further purified by recrystallization three times from acetone. mp:83~85 °C. ¹H NMR (200 MHz, CDCl₃, TMS):δ=7.6 (1H, d, Ph-CH=CH-), 7.4(2H, d, Ph-CH=CH), 6.9(2H, d, Ph-O), 6.3(1H, d, Ph-CH=CH), 4.2 (2H, t-CH₂COO), 4.0(2H, t, CH₂-O-Ph), 3.6(4H, t, CH₂-OH), 2.1(2H, t, OH), 1.3~1.7(32H, m, CH₂). Anal:Calcd. for C₂₉H₄₈O₅: C, 73.11; H, 10.08. Found:C, 72.93; H, 10.08.

1.2 Methods

1.2.1 Determination of π -A isotherms

π -A isotherms were recorded on a Krüss Filmbalance FB-1 at (30.00±0.1) °C with a compression speed of 1.3 cm·min⁻¹. The trough was cleaned by wiping the Teflon portions with chloroform and waiting for 15 min to allow all the chloroform to evaporate. The remaining contamination on the surface of the subphase was further removed by using a suction pump.

1.2.2 Fabrication of LB films

LB film depositions were carried out on Face No. 05935 with Alternate Layer Langmuir-Blodgett Trough (Type622, Serial No.024, Japan). The LB films were fabricated onto BaF₂ and quartz surface respectively by the vertical dipping method at a surface pressure of 15 mN·m⁻¹ and a dipping speed of 5.0 mm·min⁻¹.

1.2.3 XRD studies

Reflection XRD studies were carried out with a RINT-2000 X-ray diffractometer(USA). The X-ray beam was generated with a Cu anode, and the wavelength of K_{α1} beam was 0.15406 nm. The X-ray beam was directed toward the film edge, and the scanning was done up to the 2θ value of 8°.

1.2.4 Spectra measurements

UV-Vis absorption spectra were obtained on a Shimadzu UV-250 spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna-IR 750 Fourier transform spectrometer operating at 0.1 cm⁻¹ resolution.

1.2.5 Photoreaction in HDC LB films

The HDC LB films on quartz and BaF₂ were irradiated by 254 nm UV light of a low pressure mercury lamp (approximate power density 0.40 mW·cm⁻²). The distance between the irradiation source and the sample was kept at 10 cm. Absorbance change accompanying photodimerization of HDC was followed spectra photometrically with a Shimadzu UV-250.

2 Results and discussion

2.1 Formation of HDC multilayers at the air/water interface

Fig.1 shows the π -A isotherms of HDC before and after UV irradiation on the water surface at (30.0±0.1) °C. It is seen from Fig.1 that the area/molecule is 0.156 nm² before UV irradiation. This value is not only much smaller than that of some bolaamphiphiles in a bent conformation (1.0~1.5 nm²)^[24-25], but also smaller than that of alcohol^[26]. Such a low area/molecule may results either from build-up of multilayers or from partial dissolution of the molecules in the sub water phase^[27-28]. If the main reason for this phenomenon is the latter, i.e., the dissolution of HDC molecules in the sub water phase, the area/molecule will increase after UV irradiation, due to the smaller solubility of the HDC dimmers than that of the monomers. However, after 1 h irradiation, the area/molecule in Fig.1 decreased from 0.156 to 0.136 nm² and the collapse pressure rose significantly from 27 to 44 mN·m⁻¹, indicating that the molecules packed denser in the film and the film was more stable^[29-31]. These results supported the conclusion that the HDC molecules built up multilayers at

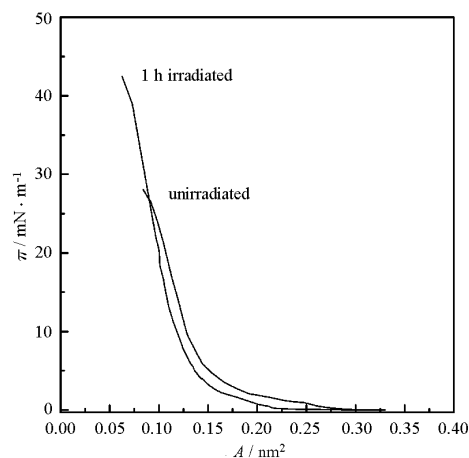


Fig.1 Surface pressure-area (π -A) isotherms of HDC multilayers at (30.0±0.1) °C

the air/water interface instead of dissolving in the sub water phase.

2.2 Photoreaction in the LB films

The multilayer structure was transferred to BaF₂ or quartz plates to fabricate LB films. Shown in Fig.2 are the UV spectra of the HDC LB films (on quartz substrate) at 25 °C. It is seen that before irradiation, the spectrum had an absorption peak at 240 nm, which dramatically blue shifted compared with that in organic solvents^[19,32]. Upon UV irradiation (254 nm), the absorption peak shifted to shorter wavelength and the absorbance decreased gradually with the increase of irradiation time, which is similar to that in the conventional cinnamic acid group containing amphiphiles OCA (4-octadecanoxycinnamic acid) LB films reported by Yang *et al.*^[18], indicating the occurrence of photoreaction in the LB films^[18,33].

The Fourier transform infrared (FT-IR) spectroscopy further proved the photodimerization of HDC molecules in the LB films (See Fig.3 and Table 1). As shown in Fig.3, after 2 h irradiation, the characteristic IR absorption bands of the monomer at 980 cm⁻¹ (CH deformation mode of trans-alkenes) and at 1632 cm⁻¹ (C=C stretching mode) disappear. In addition, the absorption at 1707 cm⁻¹ (C=O conjugated stretching mode) is replaced by a band at 1729 cm⁻¹. The newly formed band corresponds to the isolated C=O stretching mode of the ester group. It is well known that cinnamic acid and its derivatives only undergo photodimerization upon UV irradiation when the reactive centers are in highly ordered state^[17-18,20]. It seems that HDC molecules undergo photodimerization and HDC molecules assemble in the same orientation in the LB films. In fact, the dramatic blue

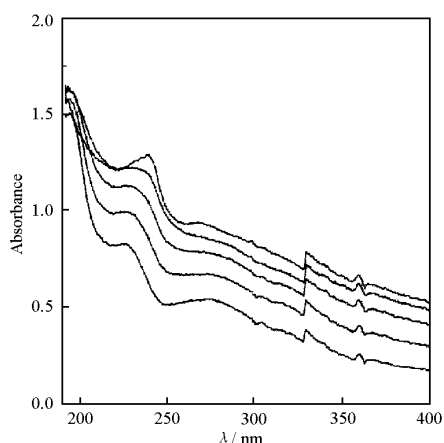


Fig.2 UV Spectra changes of HDC in LB films induced by UV irradiation

Irradiation time (from the top to the bottom): 0, 15, 30, 45, 60 min, respectively

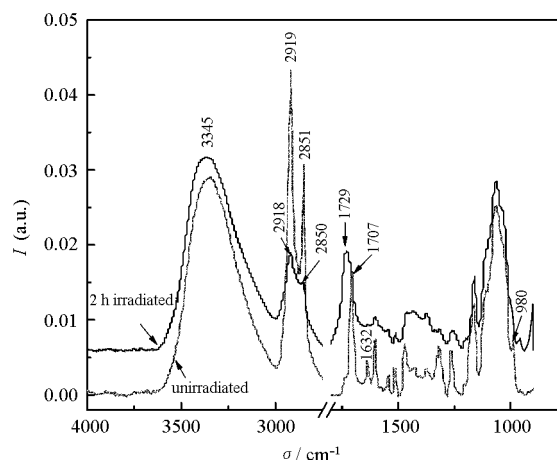


Fig.3 IR spectra of HDC LB film before and after 2 h irradiation

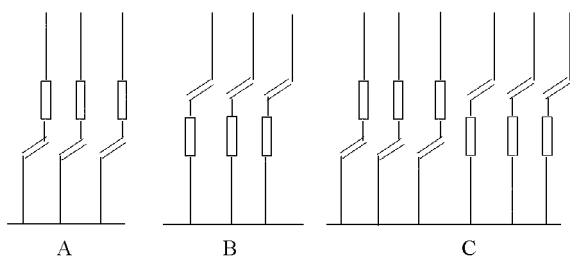
shift of absorption peak in the UV spectra indicated that the aromatic groups were stacked closely by π - π interaction^[18-34], which is consistent with the results of π -A isotherms.

It is known that the frequencies of CH₂ asymmetric and symmetric stretching vibration bands are sensitive to the degree of conformational order of alkyl chains^[35-37]. When the alkyl chains are highly ordered (trans or zigzag stretching conformation), the bands appear near 2920 and 2850 cm⁻¹, respectively; however, the bands will shift to higher wavenumbers if conformational disorder or bent mode is included in chains. From Fig.3, the asymmetric and symmetric CH₂ stretch vibration wavenumbers became lower after 2 h UV irradiation, which demonstrated that the polymethylene hydrocarbon chains of HDC in the LB films were orderly packed with all zigzag stretching conformation and packed more orderly after UV irradiation^[35-37].

Summarizing the results of UV-Visible and FT-IR spectra, most of the HDC molecules were proposed to assemble as Scheme 2A or 2B, but not as Scheme 2C in the films (Scheme 2 only demonstrated the case in monolayer). If the molecules in the HDC LB films assembled as shown in scheme 2C, the π - π stacking and part of the zigzag packing of methylene groups will be destroyed and subsequently accompanied with the decrease of the order of methylene groups, stacking mode. Thus the wavenumbers of the asymmetric and symmetric vibration

Table 1 Spectra changes of HDC before and after UV irradiation in its LB films

| | Before irradiation (cm ⁻¹) | After 2 h irradiation (cm ⁻¹) |
|-----------------|--|---|
| C=O | 1707 | 1729 |
| C=C | 1632 | weak absorption |
| C=C-H | 980 | disappeared |
| CH ₂ | 2919, 2851 | 2918, 2850 |



Scheme 2 Possible arrangement of HDC molecules in the LB films

mode in the IR spectra will increase after UV irradiation which contravene the experimental results. So the HDC molecules in the LB film are arranged as Scheme 2A or 2B. These experimental results demonstrated the superior separated group recognition of CH_2 and π - π interaction in the HDC LB films. However, it is difficult to determine whether the LB films are of A or B mode (Scheme 2) based on the current experimental results.

The mixed LB films of HDC and 1,16-hexadecanediol (98%, Aldrich Chem. Co.) were also prepared to investigate the group recognition of CH_2 and π - π interaction. The molar ratio of HDC and 1, 16-hexadecanediol was controlled to be 1:3. It has been reported that α,ω -diols or diacids adopted upstanding conformation and formed multilayer at the air/water interface^[38-39], and then the 1, 16-hexadecanediol molecules are expected to be upright as well as HDC. As a result, the time dependent spectra of HDC changed in the mixed LB films upon UV irradiation (shown in Fig.4) was similar to that of the HDC LB films (see Fig.2), indicating the occurrence of photodimerization of HDC in the mixed LB films.

From calculation based on the Chem3D modeling, the length of the upright 1, 16-hexadecanediol is about 2.24 nm (after energy minimized with MM2) and the maximum distance from the hydroxyl to the C=C bonds in the HDC molecules is 2.00 nm (Scheme 2B). Thus the 1,16-hexadecanediol molecule is long enough to inhibit the dimerization of C=C bonds from two adjacent HDC molecules. Therefore, the photodimerization will not occur if the two kinds molecules distribute randomly since the number of 1,16-hexadecanediol is triple that of HDC

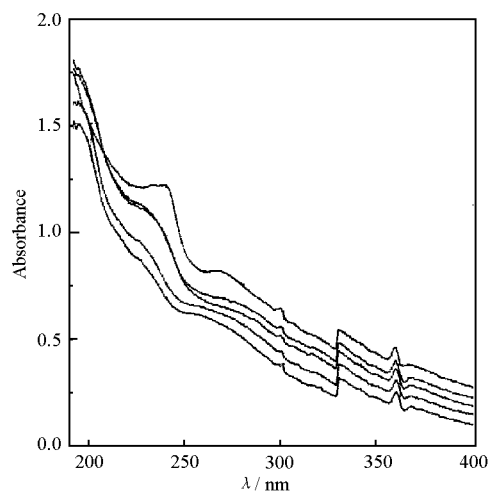


Fig.4 Change of UV spectra in the mixed LB films of HDC and 1, 16-hexadecanediol

$n(\text{HDC}):n(1,16\text{-hexadecanediol})=1:3$; UV irradiation time (from the top to the bottom): 0, 15, 30, 45, 60 min

molecules. However, the occurrence of photodimerization of HDC in the mixed films demonstrated that the phase separation occurred between the 1,16-hexadecanediol and HDC molecules. This may be attributed to the existence of two different separated interactions: π - π interaction and the zigzag stacking of methylene groups. Similar dimerization was also found by Sawaki *et al.*^[40], in the dimethyldioctadecylammonium bromide vesicle doped cinnamic acid, indicating phase separation occurred between these two kinds molecules.

2.3 Structure of the multilayer studied with XRD

The HDC LB film was also investigated by XRD to determine the period of the multilayers. The Bragg diffraction peak shown in Fig.5a and 5b indicated the existence of an ordered layer structure in the films. The long interlayer spacing obtained from diffraction peak indicates that the bilayers are formed. The calculated value^[41] of $d = 3.68$ nm is obtained by the sum of $m+4$ times of C-C bond length (0.125 nm) and the terminal O-H bond (0.06 nm) projected on the axis of the chains, with the length of cinnamic acid part, 0.56 nm (estimated from its geometric structure). Here m is the number of carbon atoms in the alkyl group, and the ether group is counted as methylene unit. In addition,

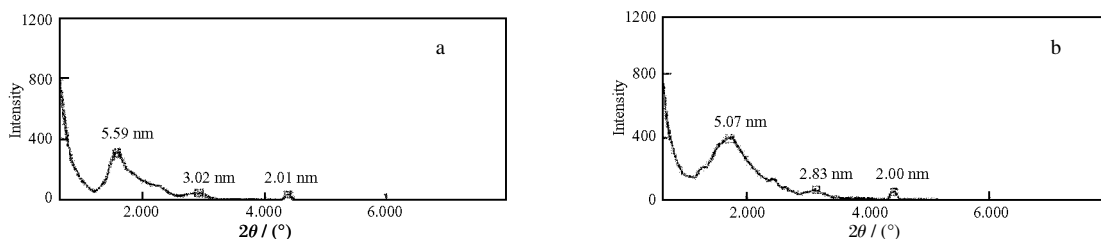
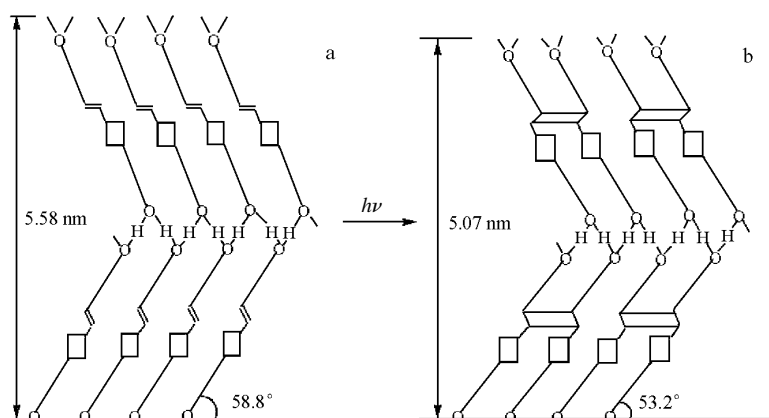


Fig.5 XRD patterns of HDC LB film before (a) after (b) 2 h UV irradiation



Scheme 3 Schematic diagram of the bilayer structures of HDC in the LB films

the length of HDC is estimated to be 3.71 nm from Chem3D. The coefficient of 2.79 nm ($5.59/2$) in XRD implies that there was a tilt angle of the hydrocarbon chains in HDC films, which value is $\arcsin(2.79/3.71)=58.8^\circ$. After UV irradiation, the ordered peaks still existed but the longest interlayer distance de-creased to 5.07 nm, corresponding to the tilt angle of $\arcsin(2.54/3.71) = 53.2^\circ$. Considering that strong hydrogen bonds (3345 cm^{-1}) also existed in the films based on the IR experimental results in Fig.3, possible arrangements of HDC molecules in LB films are suggested as Scheme 3. It should be pointed out that the second or other layers maybe in the upside down orientation as shown in Scheme 2A.

3 Conclusions

A new photoreactive bolaamphiphile HDC containing cinnamic group was synthesized. π -A isotherms revealed the build-up of multilayers of HDC at air/water interface. It was found that HDC dimerized in the LB films upon UV irradiation, indicating an upright oriented packing of HDC in the films. The phase separation in the mixed LB films of HDC and 1,16-hexadecanediol was also observed based on the UV spectra results, suggesting that strong π - π interaction and the zigzag stacking of methylene existed in the LB films. In addition, hydrogen bond was formed in the LB films. The structure of LB films before UV irradiation was finally proposed to be double molecular layer with a tilt angle of 58.8° . And the angle decreased to 53.2° after irradiation.

References

- 1 Fuhrhop, J.H.; Spiroski, D.; Boettcher, C. *J. Am. Chem. Soc.*, **1993**, **115**: 1600
- 2 Escamilla, G. H.; Newkome, G. R. *Angew. Chem., Int. Ed. Engl.*, **1994**, **33**: 1937
- 3 Franceschi, S.; Andreu, V.; Viguierie, N. de; Riviere, M.; Lattes, A.; Moisand, A. *New J. Chem.*, **1998**, **22**: 225
- 4 Yan, Y.; Huang, J. B.; Li, Z. C.; Han, F.; Ma, J. M.; Fu, H. L.; Ye, J. P. *J. Phys. Chem. B*, **2003**, **107**: 1479
- 5 Zana, R.; Levy, H. J. *Colloid Interface Sci.*, **1995**, **170**: 128
- 6 Clary, L.; Gadras, C.; Greiner, J.; Rolland, J.P.; Santaella, C.; Vierling, P.; Gulik, A. *Chemistry and Physics of Lipids*, **1999**, **99**: 125
- 7 Fuhrhop, J.H.; Spiroski, D.; Boettcher, C. *J. Am. Chem. Soc.*, **1993**, **115**: 1600
- 8 Franceschi, S.; Viguierie, N.de; Riviere, M.; Lattes, A. *New J. Chem.*, **1999**, **23**: 447
- 9 Yan, Y.; Huang, J. B.; Li, Z. C.; Han, F.; Ma, J. M. *Langmuir*, **2003**, **19**: 972
- 10 Lu, Q.; Liu, M. L. *Chinese Chem. Lett.*, **2001**, **12**: 1105
- 11 Zana, R.; Levy, H. J. *Colloid Interface Sci.*, **1995**, **170**: 128
- 12 Menger, F. M.; Wrenn, S. *J. Phys. Chem.*, **1974**, **78**: 1387
- 13 Yasuda, M.; Ikeda, K.; Esumi, K.; Meguro, K. *Bull. Chem. Soc. Jpn.*, **1989**, **62**: 3648
- 14 Huang, J. B.; Yan, Y.; Li, Z. C.; Zhao, X. L.; Zhu, B.Y.; Ma, J. M. *J. Colloid Interface Sci.*, **2003**, **258**: 206
- 15 Roberts, G. G. *Langmuir-Blodgett films*. New York: Plenum Press, 1990
- 16 Ulman, A. *An introduction to ultrathin organic films*. Boston: Academic MA Press, 1991
- 17 Quina, F. H.; Whitten, D. G. *J. Am. Chem. Soc.*, **1977**, **99**: 877
- 18 Xia, Q.; Feng, X. S.; Mu, J.; Yang, K. Z. *Langmuir*, **1998**, **14**: 3333
- 19 Koch, H.; Laschewsky, A.; Ringsdorf, H.; Teng, K. *Makromol. Chem.*, **1986**, **187**: 1843
- 20 Schmidt, G. M. *J. Chem. Soc.*, **1964**, **385**: 2014
- 21 Kawatsuki, N.; Takatani, K.; Yamamoto, T.; Ono, H. *Polym. J.*, **1998**, **30**: 946

- 22 Tieke, B.; Enkelmann, V.; Kapp, H.; Lieser, G.; Wegner, G. J. *Macromol. Sci.-Chem.*, **1981**, **A15**: 1045
- 23 Chong, J. M.; Heuft, M. A.; Rabbat, P. J. *Org. Chem.*, **2000**, **65**: 5837
- 24 Moroi, Y.; Matuura, R.; Tanaka, M.; Murata, Y.; Aikawa, Y.; Furutani, E.; Kuwamura, T.; Takahashi, H.; Inokuma, S. *J. Phys. Chem.*, **1990**, **94**: 842
- 25 Zana, R.; Yiv, S.; Kale, K. M. *J. Colloid Interface Sci.*, **1980**, **77**: 456
- 26 Lin, S. Y.; Hwang, W. B.; Lu, T. L. *Colloids and Surface A: Physicochemical and Engineering Aspects*, **1996**, **114**: 143
- 27 Adam, N. K.; Jessop, F. *Proc. Roy. Soc.*, **1926**, **A112**: 362
- 28 Böhm, C.; Leveiller, F.; Jacquemain, D.; Möhwald, H.; Kjaer, K.; Als-Nielsen, J.; Weissbuch, I.; Leiserowitz, L. *Langmuir*, **1994**, **10**: 830
- 29 Bubeck, C. *Thin Solid Films*, **1988**, **160**: 1
- 30 Day, D.; Ringsdorf, H. J. *Polym. Sci. Polym. Lett.*, **1978**, **16**: 205
- 31 Hupfer, B.; Ringsdorf, H.; Schupp, H. *Chem. Phys. Lipids*, **1983**, **33**: 355
- 32 Tanaka, Y.; Nakayama, K.; Iijima, S.; Shimizu, T.; Maitani, Y. *Thin Solid Films*, **1985**, **133**: 165
- 33 Matsusaki, M.; Kishida, A.; Stainton, N.; Ansell, C. W. G.; Akashi, M. *J. Appli. Polym. Sci.*, **2001**, **82**: 2357
- 34 Geiger, H. C.; Perlstein, J.; Lachicotte, R. J.; Wyrozebski, K.; Whitten, D. G. *Langmuir*, **1999**, **15**: 5606
- 35 Penner, T. L.; Schildkraut, J. S.; Ringsdorf, H.; Schuster, A. *Macromolecules*, **1991**, **24**: 1041
- 36 Naselli, C.; Swalen, J. D.; Rabolt, J. F. *J. Chem. Phys.*, **1989**, **90**: 3855
- 37 Umemura, J.; Kamata, T.; Kawai, T.; Takenaka, T. *J. Phys. Chem.*, **1990**, **94**: 62
- 38 Popovitz-Biro, R.; Majewski, J.; Margulis, L.; Sohen, S.; Leiserowitz, L.; Lahav, M. *J. Phys. Chem.*, **1994**, **98**: 4970
- 39 Yamamoto, M.; Furuyama, N.; Itoh, K. *J. Phys. Chem.*, **1996**, **100**: 18483
- 40 Nakamura, T.; Takagi, K.; Sawaki, Y. *Bull. Chem. Soc. Jpn.*, **1998**, **71**: 909
- 41 Song, J.; Cheng, Q.; Kopta, S.; Stevens, R. *J. Am. Chem. Soc.*, **2001**, **123**: 3205

一新种型含肉桂酸的Bola型两亲分子在LB膜中的分子排列和分子识别*

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摘要 制备了一种含肉桂酸基团的Bola型两亲分子HDC(4-(10-羟基癸氧基)-10-羟基癸氧基肉桂酸酯). 该分子在空气/水界面形成多分子层 Langmuir 膜结构. 紫外光照可使膜中 HDC 分子发生光致二聚, 也可使 HDC 与 1, 16-十六碳二醇形成的混和膜中 HDC 分子发生二聚. 光照前后膜中分子倾角分别为 58.8°和 53.2°. 从实验结果推测了分子排列模型, 认为 HDC 分子在 LB 膜中有序排列, 这来源于分子间 π - π 相互作用和疏水亚甲基链的 Z 型构象堆积.

关键词: Bola型肉桂酸衍生物, LB膜, 光致二聚, 分子排列, 分子识别

中图分类号: O647.2