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Effect of Temperature on Aggregation Structure of LB Film

Seiji TONE, † Masashi KUNITAKE, †† Motoko UCHIDA, Toyoki KUNITAKE, and Tisato KAJIYAMA*
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University,
6-10-1, Hakozaki, Higashi-ku, Fukuoka 812

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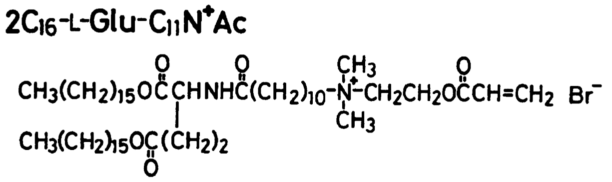
Synopsis. Molecular assembly of polymerizable amphiphile ([2-(acryloyloxy)ethyl][10-[*N*-[1,3-bis(hexadecyloxycarbonyl)propyl]carbanoyl]decyl]dimethylammonium bromide, designated as dihexadecyl *N*-[11-[[2-(acryloyloxy)ethyl]dimethylammonio]undecanoyl]glutamate bromide, $2C_{16}$–L-Glu–$C_{11}N^+Ac$) in the LB film was investigated in the temperature range above and below of the crystal–liquid crystal phase transition on the basis of wide-angle X-ray diffraction measurements. The crystal–liquid crystal phase transition temperature, T_c was determined to be 323 k based on differential scanning calorimetry (DSC). The LB film was in the form of highly oriented bilayer lamella and hexagonally assembled cylinder (rod) structure below and above T_c of the LB film, respectively. The hexagonally assembled cylinder structure above T_c may be formed due to the reason why a hydrophobic part occupies much larger cross-sectional area in comparison with that of a hydrophilic part above T_c. The change of bilayer lamella-hexagonally assembled cylinder was thermally reversible beyond T_c.

Langmuir–Blodgett (LB) films[1)] are prepared by the successive deposition of monolayers on the water surface onto solid substrate. LB films can be a candidate for the functional applications because the thin films are composed of amphiphilic molecules with molecularly designed architecture. In fact, the LB film of polymerized amphiphiles showed excellent biocompatibility (blood compatibility) because the optimal surface chemical structure for blood compatibility could be designed by using the LB method and also, could be immobilized by polymerizing the reactive group of amphiphile molecule.[2,3)] The temperature dependence of molecular assembly, especially beyond the thermal phase transition, in the LB film should be studied in order to obtain a temperature stable or a temperature sensitive functional ultra-thin film. In this study, molecular assembly of the polymerizable amphiphile in the LB film was investigated in the temperature ranges above and below the crystal–liquid crystal phase transition on the basis of X-ray diffraction measurements.

Experimental



$$\mathrm{CH_3(CH_2)_{15}O\overset{O}{\overset{\|}{C}}\underset{CH_3(CH_2)_{15}O\underset{\underset{O}{\|}}{C}(CH_2)_2}{\underset{|}{C}}HNH\overset{O}{\overset{\|}{C}}(CH_2)_{10}\text{-}\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}\text{-}CH_2CH_2O\overset{O}{\overset{\|}{C}}CH{=}CH_2\ Br^-}$$

Fig. 1. Chemical structure of polymerizable amphiphile, $2C_{16}$–L-Glu–$C_{11}N^+Ac$.

Figure 1 shows the chemical structure of polymerizable amphiphile, [2-(acryloyloxy)ethyl][10-[*N*-[1,3-bis(hexadecyloxycarbonyl)propyl]carbanoyl]decyl]dimethylammonium bromide. We call this amphiphile as dihexadecyl *N*-[11-[[2-(acryloyloxy)ethyl]dimethyl ammonio]undecanoyl]-glutamate bromide ($2C_{16}$–L-Glu–$C_{11}N^+Ac$)). The detail of synthesis of $2C_{16}$–L-Glu–$C_{11}N^+Ac$ has been reported elsewhere.[4)] A chloroform solution of $2C_{16}$–L-Glu–$C_{11}N^+Ac$ of 0.1 mg ml^{-1} was spread on the water surface at 289 K. The monolayer was transferred by the vertical dipping method[1)] onto the polystyrene film substrate with 30 μm thick, at the surface pressure of 29.5 $mN\,m^{-1}$. The crystal–liquid crystal phase transition behavior of LB film was studied by a DSC measurement. Molecular assembly in the LB film was investigated on the basis of X-ray diffraction studies.

Results and Discussion

Figure 2 shows the DSC curve of the $2C_{16}$–L-Glu–$C_{11}N^+Ac$ LB film. The DSC curve showed an endothermic peak at 323 K which corresponded to the crystal–liquid crystal phase transition temperature, T_c of the LB film.

Figures 3a and 3b show the X-ray diffraction patterns and their schematic representations of LB films at 297 K below T_c and at 335 K above T_c, respectively. The

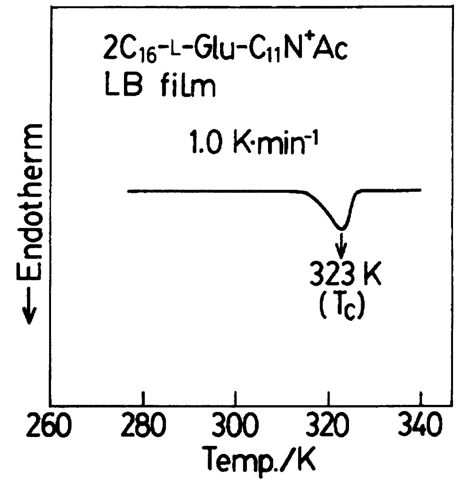


Fig. 2. DSC curve of $2C_{16}$–L-Glu–$C_{11}N^+Ac$ LB film.

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†Present address: Central Research Laboratory, Mitsubishi Rayon Co., Ltd., Miyuki-cho, Ohtake 739-06.

††Present address: Department of Industrial Chemistry, Nagasaki University, Bunkyo-machi, Nagasaki 852.

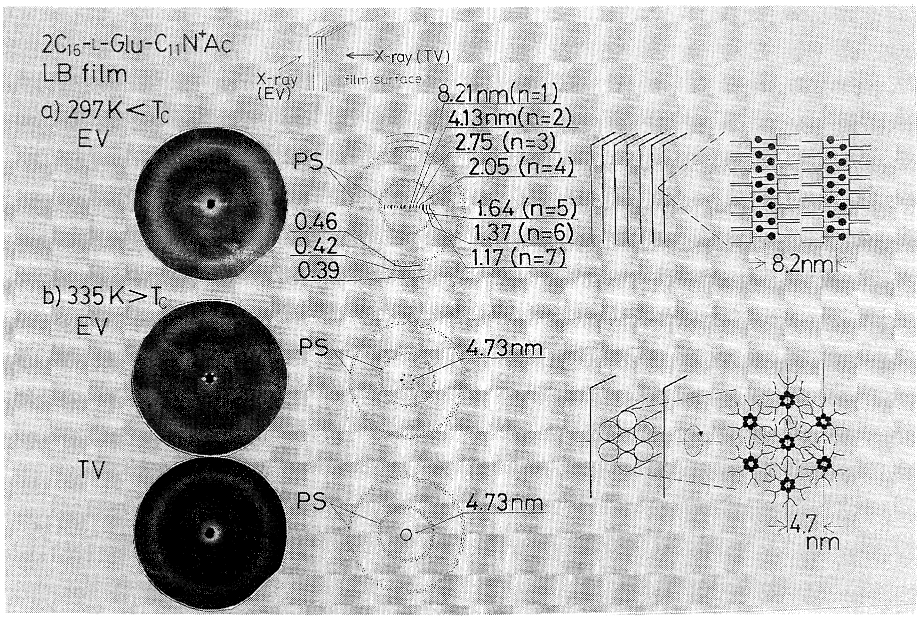

Fig. 3. X-ray diffraction patterns and their schematic representations of aggregation structure of LB films at 297 K below T_c (a), and at 335 K above T_c (b). The X-ray beam was parallel (EV) or perpendicular (TV) to the film surface.

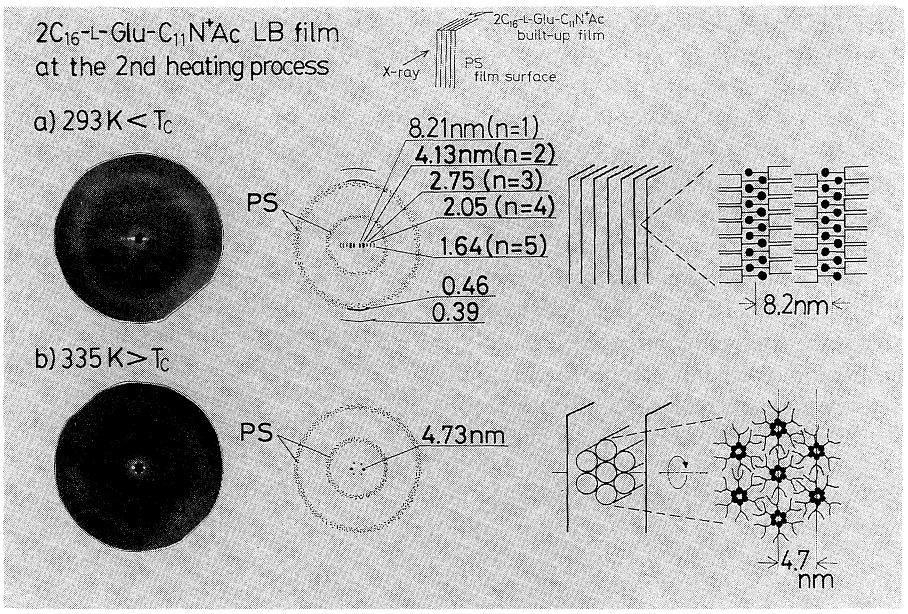

Fig. 4. X-ray diffraction patterns and their schematic representations of aggregation structure of LB film at the second heating process, at 293 K below T_c (a) and at 335 K above T_c (b). The X-ray beam was parallel to the film surface.

incident X-ray beam was parallel (edge view; EV) or perpendicular (through view; TV) to the film surface as shown in the upper part of Fig. 3. In the case of the LB film at 297 K below T_c, small angle scattering patterns with the spacings of 8.21, 4.13, 2.75 nm ... were observed on the equator, when the incident X-ray beam was irradiated parallel to the film surface. Since the reciprocal ratio of these spacings is 1 : 2 : 3 ..., it is apparent that the LB film forms the lamellar structure with the long spacing of 8.2 nm. The diffractions corresponding to the intermolecular distance of alkyl chains were also observed as arcs on the meridian, indicating that the alkyl chains were packed almost perpendicular to the built-up layers in a crystalline state. The value of long spacing, 8.2 nm is fairly shorter than the bimolecular length of $2C_{16}$–L-Glu–$C_{11}N^+Ac$, 9.1 nm calculated by the Coury–Pauling–Koltun (CPK) model. It can be reasonably expected that the hydrophilic groups of $2C_{16}$–L-Glu–$C_{11}N^+Ac$ molecules insert each other being represented by the schematic bilayer assembly as shown in the right-hand side of Fig. 3a, in order to match the cross-sectional areas of the hydrophobic part of two alkyl chains and the polar head, because the $2C_{16}$–L-Glu–$C_{11}N^+Ac$ molecule has a long spacer (C_{11}) between the hydrophilic polar head and two long alkyl chains (C_{16}). As a possible molecular assembly in the LB film below T_c, it is apparent from the X-ray patterns of Fig. 3a that the built-up layers are parallel to the film surface, and the molecular axes are oriented perpendicular to the built-up layer. On the other hand, in the case of the LB film at 335 K above T_c, the hexagonal pattern with the spacing of 4.7 nm and no diffractions corresponding to the inter-alkyl chain distance of around 0.46 nm were observed in the X-ray EV diagrams. From this result, it can be considered that the LB film at 335 K forms either a hexagonally assembled structure or a lamellar structure in which a lamellar plane bends like a trapezoid wave. Meanwhile, the slightly broadened Debye ring with the spacing of 4.7 nm and no diffractions corresponding to the inter-alkyl chain distance were observed in the X-ray TV diagrams. This Debye ring indicates that the LB film forms the hexagonally assembled structure rather than the bending lamellar structure. From these results, the schematic representation of possible molecular assembly in the LB film above T_c is shown in the right-hand side of Fig. 3b. The rod assembly with the hydrophilic cylindrical axis pack hexagonally in the plane perpendicular to the film surface, and the cylindrical axes orient randomly in the plane parallel to the film surface. Since the thermal expansion of the hydrophobic part is more remarkable in comparison with that of the hydrophilic polar part, owing to the active thermal molecular motion of alkyl chains above T_c, it is reasonable to consider that the bilayer structure of Fig. 3a must transfer to the hexagonal array of amphiphic cylinder. In the X-ray EV diagrams, the X-ray intensity for the diffraction on the equator was stronger than other four off-equator ones. This is due to that the cylindrical axes orient randomly in the plane parallel to the film surface.

Figure 4 shows the X-ray diffraction patterns and their schematic representations of molecular assembly in the LB film at the second heating process after cooling the specimen from a temperature above T_c. The X-ray beam was parallel to the film surface as shown in the upper part of Fig. 4. Figures 4a and 4b apparently indicate that the structural transformation of bilayer lamella-hexagonally assembled cylinder occurs reversibly beyond the crystal–liquid crystal phase transition temperature.

Conclusion

The transformation of molecular aggregation structure of LB film from the bilayer lamella to the hexagonally assembled cylinder with the hydrophilic cylindrical axis has been observed at T_c. This structural transformation of bilayer lamella-hexagonally assembled cylinder occurred reversibly beyond T_c. It can be considered that the hexagonally assembled cylinder above T_c of LB film is due to the thermal expansion of hydrophobic chain induced by the thermal molecular motion above T_c, which is more remarkable in comparison with that of the hydrophilic polar part.

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