Surface Stability and Functional Property of Polymerized Langmuir–Blodgett Type Films

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ABSTRACT: Langmuir–Blodgett (LB) type films, showing highly ordered layer structures, were prepared from two types of polymerizable amphiphiles. One type of the amphiphiles has a polymerizable group in a hydrophilic part, dihexadecyl *N*-[11-[[2-(acryloyloxy)ethyl]dimethylammonio]undecanoyl]glutamate bromide ($2C_{16}$-L-Glu-$C_{11}N^+Ac$), and the other has a polymerizable group in a hydrophobic part, 3-[[11-(methacryloyloxy)undecyl]dodecylmethylammonio]propanesulfonate ($MC_{11}C_{12}NS$). The LB type films composed of these amphiphiles were polymerized in order to stabilize the surface chemical structure (hydrophilicity or hydrophobicity). The highly oriented bilayer structures were kept even after polymerization. The surface chemical structure of the built-up film composed of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ was not immobilized by polymerization and the hydrophobic surface changed into the hydrophilic one in water. This result was due to that an intermonolayer polymerization hardly took place. In the case of the LB type films composed of $MC_{11}C_{12}NS$, the surface chemical structure was stabilized by polymerization and the hydrophilic surface was stable even in air. This result shows that the intermonolayer polymerization progressed in such LB type films. The blood compatibility of the built-up film composed of $MC_{11}C_{12}NS$ which has a sulfonic group in a hydrophilic part was investigated on the basis of the interaction with human blood platelets. The built-up film with sulfonic group orienting normal to the layer surface showed an excellent blood compatibility mainly owing to its negatively charged surface which repels platelets.

Introduction

LB type films prepared from amphiphiles are the organic ultrathin films with highly ordered layer structures. The LB type films are designated as both built-up films prepared by Langmuir–Blodgett (LB) method[1] and also multibilayer films cast from an aqueous solution of liposomes. The preparation method of cast multibilayer films has recently been reported.[2] The surface chemical structure (hydrophilicity or hydrophobicity) of the LB type film is easily designed by orientating the hydrophilic part or the hydrophobic part of an amphiphile on the film surface owing to the highly ordered aggregating structure of the LB type film.

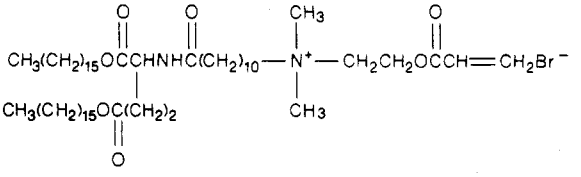
The blood compatibility is necessary for using artificial materials for biomedical purposes, for example, the diaphragm of the blood pump for artificial heart systems.[3] The blood compatibility is controlled by the interaction between the surface of the material and the surfaces of platelets, erythrocytes, and other blood components. For example, the negatively charged surface electrostatically repels these blood components which are also negatively charged.[4] In order to give an excellent blood compatibility to the material which has an excellent mechanical property, the modification of the material surface is required.[5,6] For surface modification without any change of the mechanical bulk properties of materials, the LB method is very useful. By this method, the expected surface property can be obtained owing to the highly ordered aggregating structure of LB type film.

However, the surface chemical structure of LB type film is very unstable. Molecules at the outermost surface of LB type films are generally apt to reorganize. That is, the hydrophobic parts of the molecules orient to the film surface on exposure of the film surface to air, and the hydrophilic parts of them orient to the film surface on dipping it in the water. The lack of mechanical strength of LB type films can be overcome by polymerizing the reactive groups within the amphiphiles.[7] It has been reported that polymerized built-up films[8] and cast multibilayer films[9] had sufficient mechanical strength for gas permeation experiments. It is expected that the surface chemical structure of LB type films also can be stabilized by polymerization.

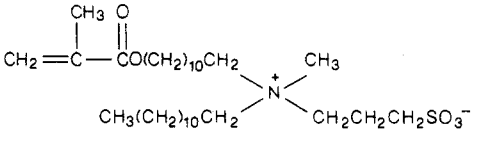
In this study, the immobilization of surface chemical structure of LB type films by photopolymerization was investigated by using amphiphiles with polymerizable groups either in a hydrophilic part or in a hydrophobic part. The blood compatibility of these LB type films composed of zwitterionic polymerizable amphiphile was also studied.

Experimental Section

Preparation of Amphiphiles. $2C_{16}$-L-Glu-$C_{11}N^+Ac$ and $MC_{11}C_{12}NS$ were used for preparation of LB type films.



$2C_{16}$-L-Glu-$C_{11}N^+Ac$



$MC_{11}C_{12}NS$

Dihexadecyl *N*-[11-[[2-(acryloyloxy)ethyl]dimethylammonio]undecanoyl]glutamate bromide ($2C_{16}$-L-Glu-$C_{11}N^+Ac$) is an amphiphile with a polymerizable group in a hydrophilic part. The details of the synthesis of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ were reported in our recent paper.[10]

3-[[11-(Methacryloyloxy)undecyl]dodecylmethylammonio]-propanesulfonate ($MC_{11}C_{12}NS$) is an amphiphile with a polymerizable group in a hydrophobic part. This amphiphile was synthesized by the four steps shown in Figure 1. 11-Bromo-1-undecanol, 10 g (39 mmol), and 10.8 g (58 mmol) of dodecylamine were added to 50 mL of ethanol with 8.2 g (77 mmol) of Na_2CO_3 and the mixture was refluxed for 72 h. Ethanol was evaporated at a reduced pressure after inorganic salt was filtrated. The

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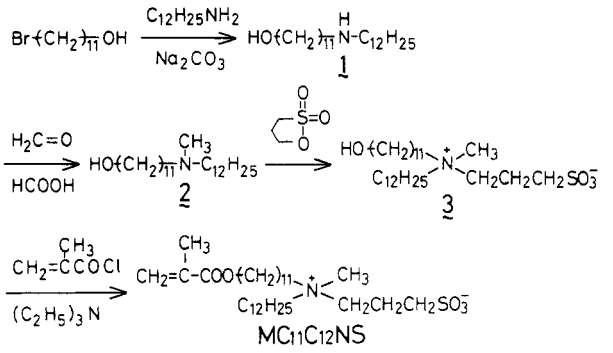

Figure 1. Method of synthesis of $MC_{11}C_{12}NS$.

residue was dissolved in 200 mL of chloroform, washed with 50 mL of concentrated aqueous NaOH five times, and dried. After evaporation of the solvent, the crude product was purified by recrystallization from methanol to give **1** (3.8 g, 28% yield). **1**, 3.8 g (11 mmol), was dissolved in 50 mL of ethanol and cooled in an ice bath. To this solution, 4.6 g (54 mmol) of formaldehyde (35 wt %) and 4.9 g (107 mmol) of formic acid were dropped slowly, and the mixture was refluxed for 24 h. After adding a concentrated KOH–ethanol solution to this mixture, the solvent was evaporated. The residue was dissolved in diethyl ether and the insoluble was filtered. After evaporation of the solvent, the oily product was obtained (**2**, 3.7 g, 93% yield). To a ethanol/acetone (1/2 v/v) solution of 3.7 g (9.9 mmol) of **2**, 1.5 g (12 mmol) of γ-propanesultone was dropped slowly. After refluxing for 20 h, the solvent was evaporated and the solid **3** was recrystallized from methanol (1.8 g, 36% yield). **3** (1.76 g, 36 mmol), triethylamine (2.2 g, 21 mmol), and 0.01 g of di-*tert*-butyl-*p*-cresol as an inhibitor were added to 50 mL of chloroform. To this mixture, 1.1 g (11 mmol) of acrylic chloride was added dropwise at 283 K. After stirring this mixture for 12 h at room temperature, the solvent was removed at reduced pressure. The residue was dissolved in 200 mL of chloroform, washed with 50 mL of saturated aqueous NaCl five times, and dried. After removal of chloroform, the residue was purified by recrystallization from methanol–diethyl ether to give $MC_{11}C_{12}NS$ (0.6 g, 31% yield) as white granules. $MC_{11}C_{12}NS$: mp 376 K; ^1H NMR ($CDCl_3$) δ 0.9 (m, 3 H), 1.2–1.4 (br s, 40 H), 1.9 (m, 3 H), 3.0–3.3 (m, 9 H), 3.6 (m, 2 H), 4.1 (t, 2 H), 5.5 (m, 1 H), 6.05 (m, 1 H); IR (neat) $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640, $\nu_{S=O}$ 1050 cm^{-1}. Anal. Calcd for $C_{31}H_{61}NO_5S$: C, 66.55; H, 10.91; N, 2.50. Found: C, 64.72; H, 11.23; N, 2.59.

Preparations of LB Type Films. A cast multibilayer film was formed from an aqueous dispersion of $MC_{11}C_{12}NS$ which was prepared by ultrasonication of 10–50 mg of the amphiphile in 4 mL of water by the reverse-phase evaporation method.[11] The aqueous dispersion was spread on a Teflon plate and allowed to stand for 2–3 days at 293 K and then dried at a reduced pressure to obtain a monomeric cast multibilayer film. Also, the solution for preparing a polymerized cast multibilayer film was obtained as an aqueous dispersion which was irradiated with a high-pressure mercury lamp for 20 min. Completion of the polymerization reaction was confirmed by the disappearance of vinyl protons on the basis of NMR measurements. The polymerized cast multibilayer film was obtained after evaporation of water from the polymerized dispersion of $MC_{11}C_{12}NS$.

Built-up films of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ and $MC_{11}C_{12}NS$ were prepared by the LB (vertical dipping) method[1] and the horizontal lifting method.[12] A monolayer was spread on the water subphase from a chloroform solution of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ or $MC_{11}C_{12}NS$ of 0.1 mg·mL^{-1}. The water was purified by a MilliQ-II water purification system (Millipore). The surface pressure–area diagrams were obtained by using a microprocessor-controlled film balance, FSD-25 (Sanesu Keisoku Co. Ltd.). The monolayer was transferred onto polystyrene or segmented poly(urethane urea) (SPUU) film substrate. Polystyrene and SPUU films were cast from a toluene solution and a dimethylacetamide (DMAc)/tetrahydrofuran (THF) (1/1 v/v) solution, respectively. The SPUU film substrate was used for blood compatibility tests of the built-up film. SPUU was synthesized by the method reported by Lyman et al.[13] SPUU has the characteristics of excellent mechanical properties and good blood compatibility owing to its microphase-separated structure composed of hard and soft segment domains.[14,15] The surface chemical structure of SPUU is easily modified by the building up $MC_{11}C_{12}NS$ monolayers, without change of its mechanical property. Since a $MC_{11}C_{12}NS$ molecule has a sulfonic group in its hydrophilic part, the built-up film of $MC_{11}C_{12}NS$ is expected to give negatively charged surface to the SPUU substrate. The negatively charged surface is expected to have excellent blood compatibility. Polymerization of the built-up films were carried out by photoirradiation. The completion of the polymerization reaction was confirmed by ATR-FT-IR measurements.

Characterizations of LB Type Films. The aggregation structure of LB type films was investigated by X-ray measurements. X-ray diffraction patterns of the LB type films were obtained by using a stabilized generator (Rigaku Rotaflex RU200). The surface properties of the LB type films were characterized by contact angle measurements which were carried out in air with water and CH_2I_2 droplets[16] or in water with air bubbles.[17]

As one of surface functional properties of the built-up films, the blood compatibility of the built-up film of $MC_{11}C_{12}NS$ was evaluated from the degree of interaction between human blood platelets and the surfaces of LB type films.[18] The film was immersed in a human platelet rich plasma (PRP) at 310 K for 1 h. The number of adhered and deformed platelets was determined by a scanning electron microscopic (SEM) observation.

Results and Discussion

I. Polymerization of the Amphiphile with a Polymerizable Group in a Hydrophilic Part ($2C_{16}$-L-Glu-$C_{11}N^+Ac$). Figure 2 (part 1) is the schematic representation of the preparation method of polymerized cast multibilayer films. In the case of an amphiphile with a polymerizable group in a hydrophilic part, polymerization of a multilayer liposome in the water propagates along an intramonolayer region (among amphiphiles belonging to the same layer) because of the presence of a water phase between bilayers as shown in Figure 2 (part 1). Therefore, the polymerized cast multibilayer film is composed only of intramonolayer-polymerized multilayers (I). In other words, there is no chemical bonding between neighboring monolayers. On the other hand, in the case of polymerization of a built-up film (Figure 2 (part 2)), intramonolayer (I) and/or intermonolayer (II) polymerizations are supposed to occur, because there is no water phase between neighboring monolayers. Intermonolayer polymerization (II) means that polymerization takes place between neighboring monolayers, and the neighboring monolayers are chemically bonded as shown in Figure 2 (part 2.II). When intermonolayer polymerization proceeds, the outermost polymerized monolayer can hardly be rearranged individually. Therefore, the overturning of the outermost monolayer, depending on the environment condition, does not occur. Even if molecular rearrangement occurs in the intermonolayer-polymerized bilayer, the surface chemical property does not changed. For these reasons, it is considered that the surface chemical structure of the LB type film can be immobilized by the intermonolayer polymerization (II) which is obtained in the case of the polymerized built-up film.

In the next section, the surface chemical characteristics of the polymerized built-up film were studied under different environmental conditions, such as in air or in water phases.

Aggregation Structure of the Built-up Film of $2C_{16}$-L-Glu-$C_{11}N^+Ac$. The upper part of Figure 3 shows the surface pressure–area (II-*A*) isotherm of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ monolayer on the purified water surface at 290 K. The occupied area was 0.42 nm^2·$molecule^{-1}$. This value corresponds to the cross-sectional area of the hydrophobic chains of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ packed closely. The built-up films were prepared at the subphase temperature of 290

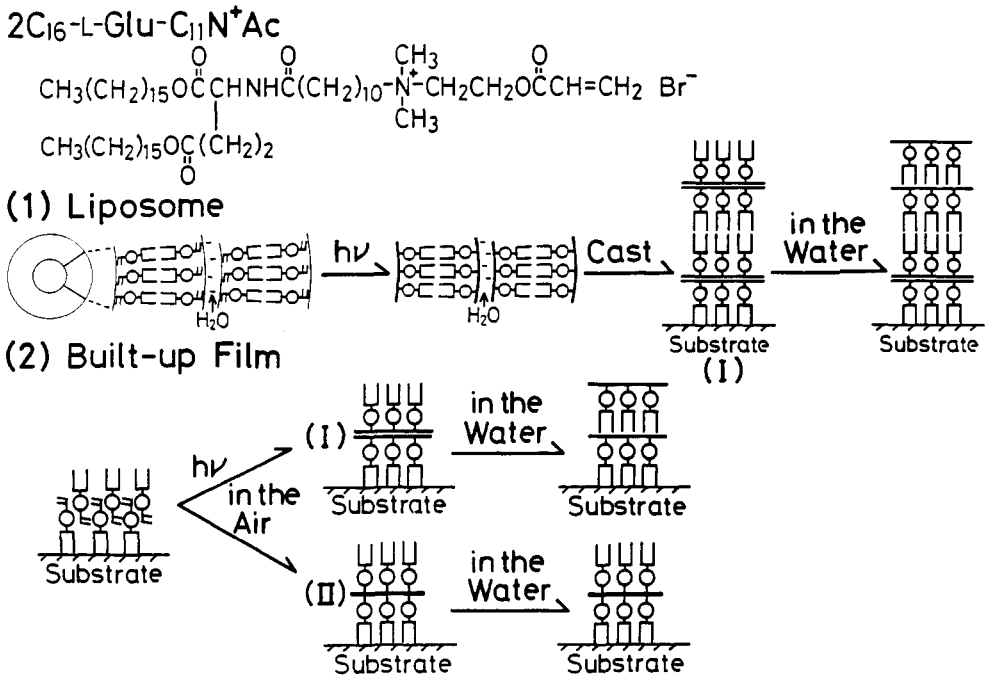

Figure 2. Chemical structure and models for polymerization of (1) a cast multibilayer film and (2) a built-up film of $2C_{16}$-L-Glu-$C_{11}N^+Ac$.

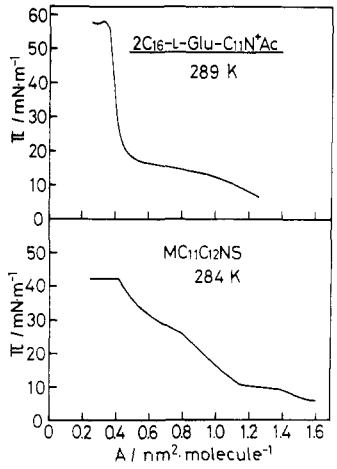

Figure 3. Surface pressure–area isotherms for monolayers of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ (upper) and $MC_{11}C_{12}NS$ (lower).

K at the surface pressure of 30 mN·m^{-1} where the monolayer was in the liquid-condensed film state. Built-up films were polymerized by photoirradiation in air.

The aggregation structures of monomeric and polymerized built-up films of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ were investigated by wide- and small-angle X-ray diffraction measurements. Figure 4 shows the wide- and small-angle X-ray diffraction patterns and their schematic representations of the monomeric (Figure 4 (part 1)) and polymerized (Figure 4 (part 2)) built-up films. The incident X-ray beam was irradiated parallel to the membrane surface which was set as shown in the upper part of Figure 4. The substrates of the built-up films were polystyrene films with thicknesses of 20 μM. In the case of the monomeric built-up film (Figure 4 (part 1)), some high-order diffractions corresponding to a long spacing of 8.2 nm were observed on the equator. This indicates that the monomeric built-up film forms the lamellar structure. The diffractions corresponding to the intermolecular distance of alkyl chains were observed as arcs on the meridian, indicating that the alkyl chains are packed perpendicular to the built-up layers. The schematic representation of possibile molecular assembly in the monomeric built-up film is shown in the right-hand side of Figure 4 (part 1). The built-up layers are parallel to the film surface, and the molecular axes are oriented perpendicular to the surface of the built-up layer. Also, in the case of the polymerized built-up film (Figure 4 (part 2)), the sharp diffractions corresponding to a long spacing of 8.0 nm were observed up to the fifth order on the equator. Diffractions corresponding to the intermolecular distance of alkyl chains were observed as arcs on the meridian. Though the long spacing contracted slightly after polymerization, the highly oriented bilayer structure was preserved even after polymerization.

Surface Stability of the Built-up Film of $2C_{16}$-L-Glu-$C_{11}N^+Ac$. The surface property of $2C_{16}$-L-Glu-$C_{11}N^+Ac$ built-up film was characterized by a contact angle measurement. Figure 5 shows the variation of underwater surface–air–water contact angles (ϕ) for the built-up film with the polymerization (irradiation) time. Polymerization was carried out in air. The contact angle was measured after immersing the specimen in the water phase for 2 min. In air, the hydrophobic groups oriented outward from the surfaces of the monomeric and polymerized built-up films. However, when the monomeric built-up film was immersed in the water, the magnitude of ϕ (filled circle in Figure 5) was smaller, indicating the hydrophilicity of the surface. This result shows that the surface chemical property of the monomeric built-up film can be easily changed depending on the environmental conditions (hydrophobic or hydrophilic). With increasing polymerization time (10–30 min) (opened circles in Figure 5), the magnitude of ϕ became larger. This indicates that the hydrophobic surfaces were immobilized even in the water phase, especially between the polymerization time of 10 and 30 min. When the polymerization time was more than 40 min, the hydrophobicity of the specimen surface decreased owing to the chemical degradation of amphiphile molecules caused by a photoirradiation. Therefore, the most suitable polymerization time for immobilizing the surface chemical structure was estimated to be 30 min.

Figure 6 shows the variation of ϕ for the built-up film photoirradiated for 30 min with immersion time in water. When the immersion time was short, the surface chemical structure of the polymerized built-up film maintained

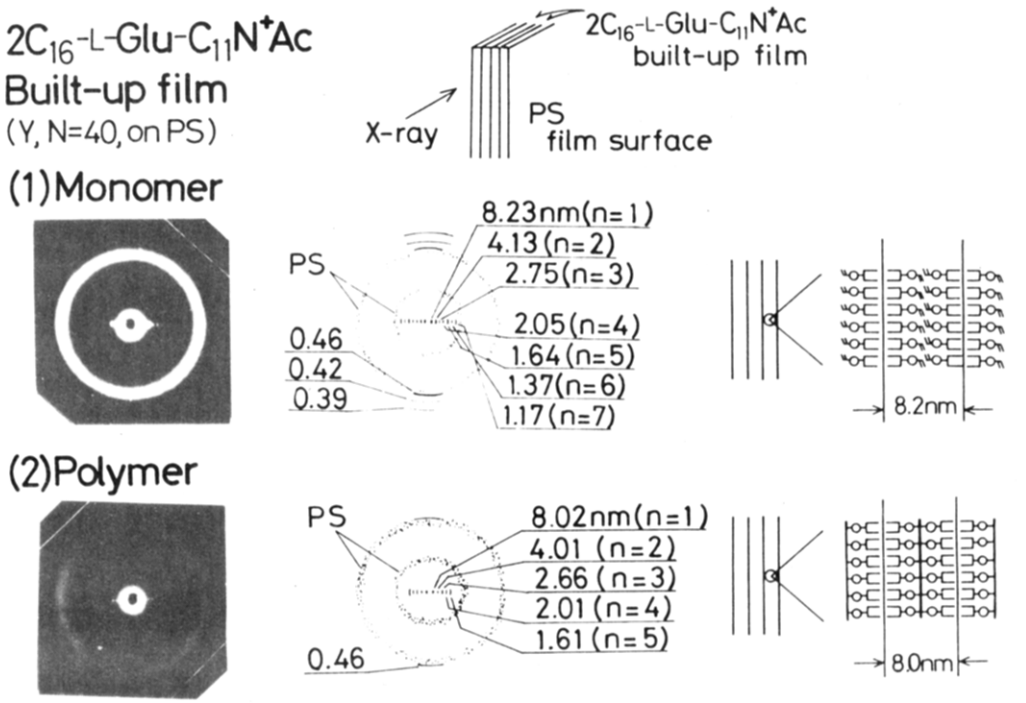

Figure 4. Wide- and small-angle X-ray diffraction patterns and schematic representations of (1) monomeric and (2) polymerized built-up films of $2C_{16}$-L-Glu-$C_{11}N^+Ac$.

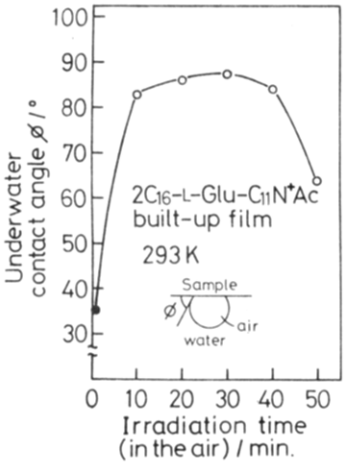

Figure 5. Variation of underwater surface–air–water contact angle for a $2C_{16}$-L-Glu-$C_{11}N^+Ac$ built-up film with polymerization time.

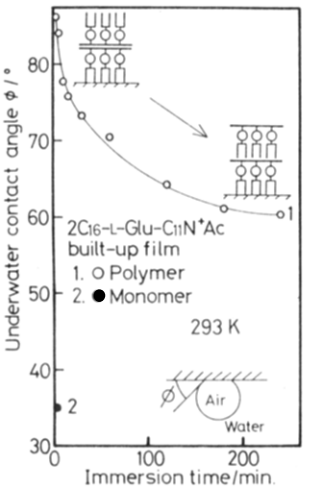

Figure 6. Variation of underwater surface–air–water contact angle for a $2C_{16}$-L-Glu-$C_{11}N^+Ac$ built-up film with time immersed in water.

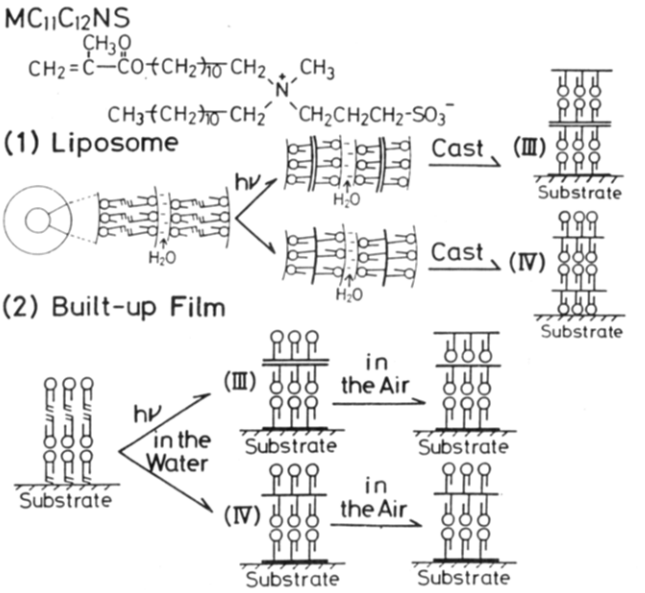

Figure 7. Chemical structure and models for polymerization of (1) a cast multibilayer film and (2) a built-up film of $MC_{11}C_{12}NS$.

hydrophobic nature even in water. However, the hydrophobic surface gradually changed into a hydrophilic one with an increase in the immersion time. This indicates that the surface chemical structure could not be completely immobilized owing to the overturning of the outermost monolayer which was polymerized in the intramonolayer region as shown in Figure 2 (part 2.I).

II. Polymerization of an Amphiphile with a Polymerizable Group in the Hydrophobic Part ($MC_{11}C_{12}NS$). Figure 7 shows the schematic representations of the preparation methods of the polymerized cast multibilayer film starting from a liposome (1) and a built-up film (2) for $MC_{11}C_{12}NS$. Intramonolayer (III) and/or intermonolayer (IV) polymerizations are capable for cast multibilayer and built-up films of $MC_{11}C_{12}NS$. If polymerization proceeds by this type of intermonolayer (IV) reaction, the surface chemical structure of the LB type

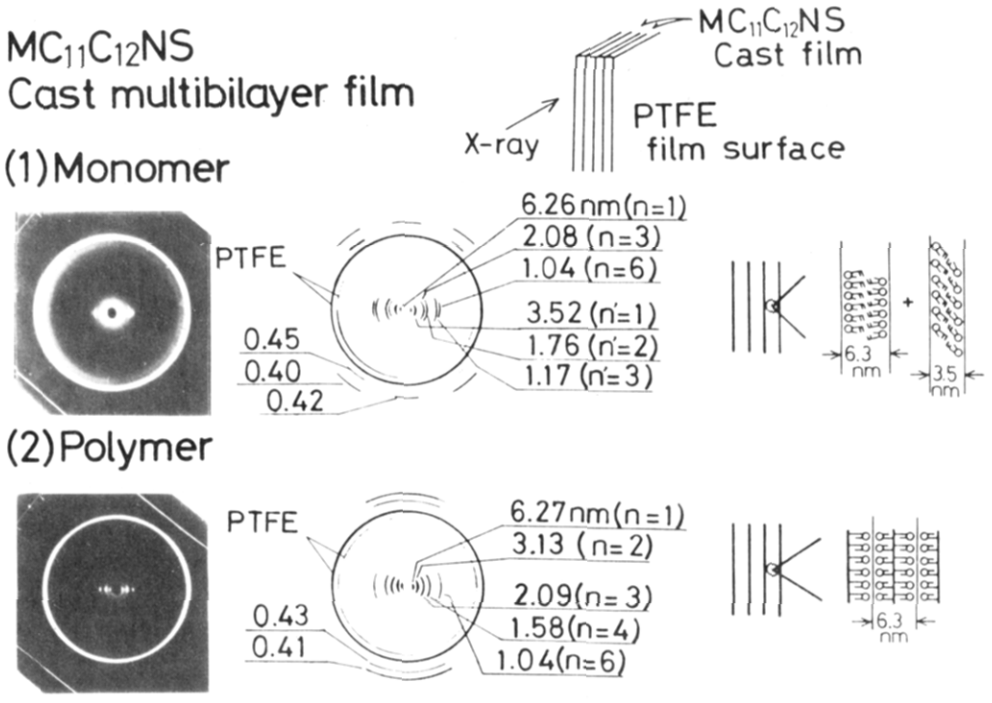

Figure 8. Wide- and small-angle X-ray diffraction patterns and schematic representations of (1) monomeric and (2) polymerized cast multibilayer films of $MC_{11}C_{12}NS$.

film can be maintained under any environmental conditions.

Aggregation Structure of the Cast Multibilayer Film of $MC_{11}C_{12}NS$. Figure 8 shows the wide- and small-angle X-ray diffraction patterns and their schematic representations for the monomeric and polymerized cast multibilayer films. The monomeric and polymerized cast multibilayer films were obtained from the monomeric liposome and the photoirradiated liposome aqueous solution, respectively. In the case of the monomeric cast multibilayer film shown in Figure 8 (part 1), sharp diffractions were observed on the equator. These patterns corresponded to the two types of layer structures with long spacings of 6.3 and 3.5 nm. For each long spacing, the ratio of reciprocal spacings on the equator were integer (1:2:3), which indicates that there are two kinds of lamella structures in the monomeric cast multibilayer film. Furthermore, wide-angle X-ray diffraction patterns showed the two types of aggregations of alkyl chains; one was observed on the meridian (0.42 nm) (perpendicular alignment of alkyl chains to the lamellar surface) and the other as four pointed interferences tilted to the meridian with an angle of 40° (0.45 and 0.40 nm) (oblique alignment of alkyl chains to the lamellar surface). A long spacing of 6.3 nm corresponds to a bimolecular length of $MC_{11}C_{12}NS$ calculated by the CPK molecular model. These results indicate that the monomeric cast multibilayer film has two types of oriented bilayer structures: one with bilayers parallel to the substrate surface with a long spacing of 6.3 nm, and molecules are packed perpendicular to the bilayers, and the other is with bilayers parallel to the substrate surface with a long spacing of 3.5 nm and molecular long axes tilt to their bilayer surfaces at 40°. The possible aggregation model in the bilayer is schematically shown in the right-hand side of Figure 8 (part 1). The different types of aggregating structures of bilayers probably derived from the chemical structure of $MC_{11}C_{12}NS$. $MC_{11}C_{12}NS$ has a polymerizable group at the end of one alkyl chain. And the length of the alkyl chain with a polymerizable group is quite different from that of the other alkyl chain with no polymerizable group. This antisymmetric structure of the alkyl chain caused the different aggregating structure of the bilayer. On the other hand, in the case of a polymerized cast multibilayer film as shown in Figure 8 (part 2), some high-order diffractions with a long spacing of 6.3 nm were observed on the equator and, also, reflections corresponding to intermolecular distances of alkyl chains were observed on the meridian. Figure 8 (part 2) indicates that the cast multibilayer film polymerized in the liposome state has one component of oriented bilayer structure and the polymerized molecules assemble perpendicular to the bilayer surface.

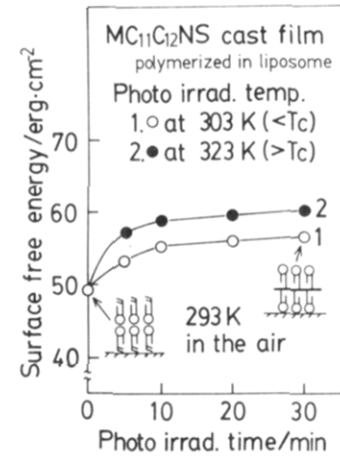

Figure 9. Variations of surface free energy of cast multibilayer films of $MC_{11}C_{12}NS$ in air with polymerization time.

Surface Stability of the Cast Multibilayer Film of $MC_{11}C_{12}NS$. The surface properties of cast multibilayer films prepared from liposome were characterized from the magnitude of surface free energy in the air which was evaluated from the contact angle measurements with water and CH_2I_2 droplets. Figure 9 shows the variations of surface free energy in the air for the cast multibilayer films with polymerization (photoirradiation in the liposome state) time. The surface free energy was calculated on the basis of the equation proposed by Owens and Wendt.[16] The polymerization of liposome proceeded in the water at

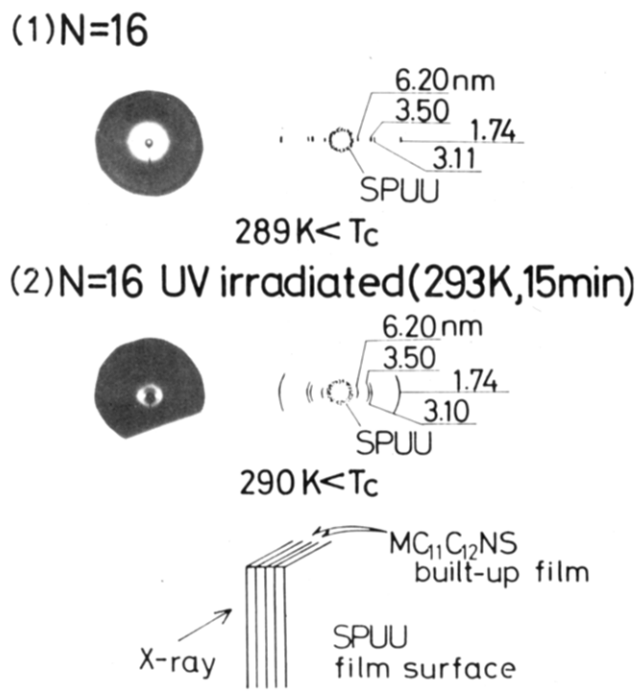

Figure 10. Small-angle X-ray scattering (SAXS) patterns and schematic representations of (1) monomeric (upper) and (2) polymerized (lower) built-up films of $MC_{11}C_{12}NS$.

a temperature below (opened circles in Figure 9) or above (closed circles in Figure 9) the crystal-to-liquid crystal phase transition temperature of liposome (T_c = 310 K). The degree of surface hydrophilicity in the air (corresponding to the greater magnitude of surface free energy) increased with an increase in the polymerization time. The polymerized hydrophilic surface was quite stable for a long time in air. These indicate that the hydrophilic surface was immobilized in air. Since the polymerized cast multibilayer film was obtained in the intermonolayer polymerized structure as shown in Figure 7 (part IV), the reorganization of the surface structure did not occur even though the hydrophilic surface was unstable in air. Figure 9 shows that the cast multibilayer film polymerized in a liquid crystalline state of liposome has more hydrophilic surface than that polymerized in a crystalline state. This result probably arises from the fact that the fraction of intermonolayer polymerization becomes larger owing to the greater mobility of molecules for positional rearrangement in the case of polymerization in a liquid crystalline state.

Aggregation Structure and Surface Stability of the Built-up Film of $MC_{11}C_{12}NS$. The lower part of Figure 3 shows the Π–A isotherm of a $MC_{11}C_{12}NS$ monolayer on the purified water subphase at 284 K. The occupied area was 0.82 nm^2·molecule^{-1}. This value agreed with the occupied area of a molecule tilting to the surface of monolayer with about 50°. The built-up films were prepared at 30 mN·m^{-1} (the liquid condensed state) and at 290 K.

Figure 10 shows the small-angle X-ray scattering (SAXS) patterns of the monomeric (upper, part 1) and the polymerized (lower, part 2) built-up films on the substrates of SPUU. The polymerized built-up film was obtained by photoirradiation of the monomeric built-up film. In the case of the monomeric built-up film (Figure 10 (part 1)), sharp diffractions were observed on the equator. These long spacings were 6.2 and 3.5 nm, which were comparable with the magnitudes of long spacings of the monomeric cast multibilayer film (Figure 8 (part 1)). As mentioned before, the bilayer with a long spacing of 3.5 nm is composed of molecules tilting to the bilayer surface at 40°,

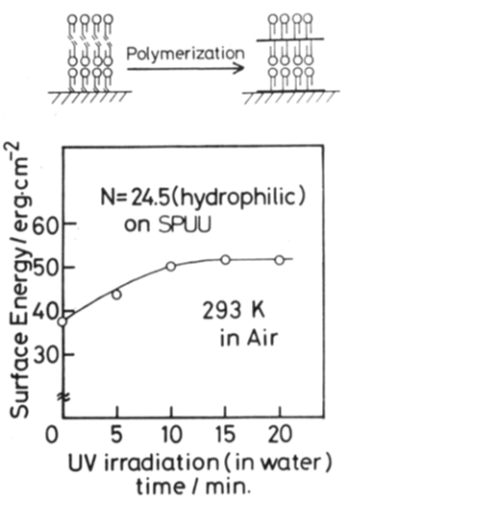

Figure 11. Variation of the surface free energy of built-up films of $MC_{11}C_{12}NS$ in air with polymerization time.

which corresponds to the magnitude of tilting angle calculated from the occupied area in the Π–A isotherm of Figure 3. In the case of the polymerized built-up film as shown in Figure 10 (part 2), the long spacings of 6.2 and 3.5 nm were also observed. However, the diffractions on the equator were slightly broad along the azimutal angle. This indicates that the degree of the bilayer orientation and/or that of the molecular orientation in the bilayer decreased owing to polymerization. As mentioned before, the polymerized cast multibilayer film (Figure 8 (part 2)) is composed of only one type of bilayer structure with long spacing of 6.3 nm. These different aggregation structures between the polymerized cast multibilayer film (Figure 8 (part 2)) and the polymerized built-up film (Figure 10 (part 2)) may occur owing to the different conditions of polymerization. That is, in the case of the cast multibilayer films, polymerization was carried out in a liposome state in the water phase, and therefore mobility or rearrangement of molecules is much greater than the polymerization in a built-up film state. Though the experimental evidence has not been obtained yet, molecules in the polymerized cast multibilayer film may assemble at the most stable aggregation state in the bilayer.

The surface properties of the built-up films were characterized by contact angle measurements in air, by using the built-up film with the hydrophilic surface polymerized in the water phase. Figure 11 shows the variation of the surface free energy of the built-up film in air with the polymerization (photoirradiation) time. N = 24.5 means that after 24 bilayers (N = 24) were built-up by the LB method, one monolayer (N = 0.5) was subsequently transfered by the horizontal lifting method to obtain the hydrophilic outermost surface. Since the hydrophilic surface is very unstable in the air, the hydrophilic surface generally has a tendency to change to the hydrophobic one after exposing the surface to the air for a while. To immobilize the hydrophilic surface in air, the built-up films (N = 24.5) were polymerized under photoirradiation in the water phase. Figure 11 shows that the hydrophilic surface was apparently immobilized even in air by polymerization in water for more than 10 min. This indicates the propagation of intermonolayer polymerization as shown in Figure 7 (part IV). In a similar fashion, the hydrophobic surface of the built-up film (N = 24) existed stably even in the water phase after polymerization in air.

Blood Compatibility of the Built-up Film of $MC_{11}C_{12}NS$. The blood compatibility was investigated as one of the surface functional properties of the built-up film.

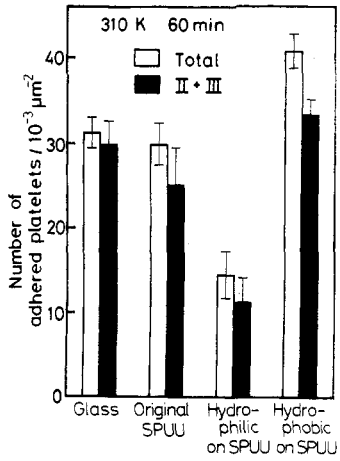

Figure 12. Number of adhered (total) and deformed (II + III) platelets on the polymerized built-up films with a hydrophobic surface (N = 10) and a hydrophilic surface (N = 10.5), showing the cases of glass and original SPUU as reference materials.

It is known that the inner wall of natural blood vessels is covered with the bilayer membranes of lipids and the surface is partially composed of mucopolysaccharides which possess anionic groups, such as sulfate and carboxylate groups.[9] It is supposed that this negative surface repels platelets, erythrocytes, and other blood components which are negatively charged. In addition, it is considered that heparin shows an excellent antithrombogenicity because it has sulfonic groups. Since $MC_{11}C_{12}NS$ has a sulfonic group in a hydrophilic part, the built-up film orienting the hydrophilic part to the outermost surface is expected to show good blood compatibility. The degree of interaction between blood platelets and the surface of the built-up film is closely related to thrombogenicity of the built-up film. The blood compatibility of the built-up film was evaluated from the number of adhered and deformed platelets on the film surface. The morphology of adhered platelets on the substratum was classified into three types owing to the degree of deformation:[14,18] (I) attachment of platelets at a point of contact with the substratum; (II) centrifugal growth of filopodia; (III) cytoplasmic webbing and flattening of the central mass.

Since the deformation of adhered platelets proceeds in order of I, II, and III with time, these morphological observations are applicable for a measure of the blood compatibility. In the case of type I, the interaction between the substrate and platelets is weak and therefore adhered platelets can be easily removed. Since the platelets of types II and III strongly adhere to the substrate, the number of adhered platelets of these types (number of deformed platelets) would be an index of thrombogenicity. Figure 12 shows the number of adhered (total) and deformed (II + III) platelets on the polymerized built-up films with the hydrophobic surface (N = 10) and with the hydrophilic surface (N = 10.5), showing the cases of glass and original SPUU as reference materials. The polymerized built-up film with a hydrophilic surface showed excellent blood compatibility in comparison with other films, especially the polymerized built-up film with a hydrophobic surface. The adhered platelets on the hydrophilic surface were not deformed and kept their native shape, indicating the weak interaction between this hydrophilic surface of the $MC_{11}C_{12}NS$ built-up film and the surface of platelets. Since $MC_{11}C_{12}NS$ had a sulfonic group in its hydrophilic part, the hydrophilic surface of the polymerized built-up film was negatively charged. The good blood compatibility of the polymerized built-up film with the hydrophilic surface is probably attributed to the weak interaction between negative charge on the membrane surface of platelets and negative charge on the surface of the built-up films.

Conclusion

In the case of an amphiphile with a polymerizable group in a hydrophilic part ($2C_{16}$-L-Glu-$C_{11}N^+Ac$), the surface chemical structure of the LB type film (built-up film) was not fixed completely by polymerization. Since polymerization proceeded in the intramonolayer region, there was enough mobility of molecules to reorganize the surface characteristics of the built-up film. In the case of an amphiphile with a polymerizable group in a hydrophobic part ($MC_{11}C_{12}NS$), the surface chemical structure of the LB type films (a built-up film and a cast multibilayer film) was immobilized by polymerization. This is ascribed to a decrease in mobility of monolayer at the surface of the LB type film, which was caused by intermonolayer polymerization. Even if the overturning occurs in the intermonolayer-polymerized bilayer, the surface chemical structure does not changed. Therefore, the hydrophilic surface in air and the hydrophobic surface in water are stable, even though they are thermodynamically unstable conditions. Excellent blood compatibility was observed for the polymerized built-up film with a negatively charged hydrophilic surface.

Registry No. 1, 119244-48-3; 2, 119244-49-4; 3, 119244-50-7; $Mc_{11}C_{12}NS$, 119273-05-1; $(MC_{11}C_{12}NS)_x$, 119273-06-2; $2C_{15}$-L-Glu-$C_{11}N^+Ac$, 107066-16-0; $(2C_{16}$-L-Glu-$C_{11}N^+Ac)_x$, 116910-53-3; $(MC_{11}C_{12}NS{\cdot}2C_{16}$-L-Glu-$C_{11}N^+Ac)_x$, 119363-37-0; $Br(CH_2)_{11}OH$, 1611-56-9; $C_{12}H_{25}NH_2$, 124-22-1; $CH_2{=}C(CH_3)COCl$, 814-68-6; γ-propanesultone, 1120-71-4.

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