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MONOLAYERS AND MULTILAYERS OF AMPHIPHILIC PHOSPHOLIPID ANALOGOUS POLY(ACRYLAMIDE)S

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ABSTRACT

A series of amphiphilic phospholipid analogous acrylamide monomers and homopolymers containing long alkyl chains as the hydrophobic groups and phosphatidylcholine analogues as the hydrophilic groups were used to study the properties of monolayers and multilayers. The P-A isotherms of the monolayers for these monomers and polymers were measured at different temperatures. The temperature and length dependence of alkyl chains, and the difference between monomers and polymers were investigated, respectively. On the other hand, the LB multilayers of all monomers and polymers were prepared. The contact angles of LB films obtained with pure water were also measured.

INTRODUCTION

Biological cell membranes are composed of lipids, proteins, and carbohydrates. The most characteristic property of lipids and proteins, from a physicochemical point of view is their amphiphilic behavior, resulting from the occurrence of a water-repelling (hydrophobic) part and a water-attracting (hydrophilic) part of the molecule. Cell exploits the amphiphilic nature to create anatomical boundaries, e.g., the plasma membrane. During the early 1960's, researchers demonstrated that certain classes of lipids, especially phospholipid, could be used to form protein- and carbohydrate-free model membrane. It has been found that the Langmuir-Blodgett (LB) technique could be used to prepare ultrathin films that have controlled thickness and orientation of molecules, and it may have the application in constructing synthetic phospholipid membrane. However, the LB films prepared from nonpolymeric amphiphiles are in general physically fragile, and they have a tendency to molecularly reorganize [1–3]. Comparatively, LB films prepared from polymeric amphiphiles are generally more stable physically, and can be expected to be less prone to reorganization. This has prompted numerous studies of monolayers and LB films of polymers in recent years [4–8].

To obtain the stable phospholipid analogous membrane artificially, we first synthesized a polymeric phospholipid analogue in 1977 [9]. For almost twenty years, a great amount of effort has been directed toward the preparations and properties of amphiphilic phospholipid analogous monomers and polymers by our and other research groups [10–18]. In addition, the monolayer and LB film of a polymeric phospholipid analogue with a methacrylamidic phosphatidylethanolamine as the hydrophilic group was investigated by Nakaya and coworkers in 1990 [19]. The report about monolayers of acrylamide monomer and polymer based on phosphatidylethanolamine was followed by Zaitsev *et al.* [20]. We recently observed the phase transitions of monolayers of some poly(acrylamide)s which were obtained from a phosphatidylcholine analogous monomer and two long alkyl chains monomers with random arrangements [15, 21]. In order to study the effect of alkyl chains on monolayers and LB films in this paper, a series of amphiphilic acrylamide monomers and homopolymers containing one different long alkyl chain as the hydrophobic group and a phosphatidylcholine analogue as the hydrophilic group, (which have proved to exist as bilayer structures in condensed phases) [22], were used for preparing monolayers and LB multilayers. The properties of these monolayers were investigated by studying their p–A isotherms at different temperatures, while their multi-layers were discussed based on their deposition ratios using the vertical dipping method. Furthermore, to study the hydrophobicity-hydrophilicity of the surface of the LB films obtained, the contact angles of LB films with pure water were measured.

EXPERIMENTAL

Materials

Chloroform, chlorobenzene, and diethyl ether were distilled over phosphorus pentoxide. Anhydrous methanol was obtained by distillation in the presence of magnesium and iodine. Acetone was dried by distillation from anhydrous potassium carbonate.

The synthesis and characterization of 2-[2-(acrylamide ethyl)dimethylammonio]ethyl alkyl phosphates have previously been described in detail [20].

Measurement

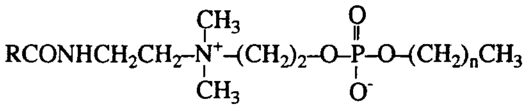
P–A isotherm measurements and LB film preparations were carried out with a computer controlled apparatus: Film–Balance Measuring (Lauda). The contact-angles of LB films with pure water were measured by a Face Contact-Angle Meter (CA-A).

Surface Pressure (P)–Area (A) Isotherms Measurements

A computer-controlled film balance apparatus was used for measuring surface pressure as a function of molecule-occupied area for monomer and unit-occupied area for polymer. The trough area is 927 cm^2, and the temperature of the aqueous subphase is maintained at ±0.1 °C centering a set temperature during the measurement. The concentration of the spreading solution was 1.0 mg/10 mL in the mixture of chlorobenzene and methanol (4/1 by volume). After 0.2 mL of the solution was spread onto the sub-phase, the monolayer film was incubated for 15 minutes and then compressed at a rate of 0.5 mm/s.

LB Films Preparations

Langmuir-Blodgett multilayers were prepared by using a commercially available film balance apparatus (Lauda) on pure aqueous subphase (pH=5.8) at 20°C. Multilayers were deposited on poly(ethylene terephthalate) (PET) plates with the vertical dipping method. The hydrophobic support materials PET plates were cleaned by ultrasonication in chloroform, washed with diethyl ether, and then rinsed with distilled water several times. LB depositions were performed at a surface pressure of P=15 mN/m for monomer **1** and 30 mN/m for the others with a down- and up-ward speed of 20 mm/min. The amount of consumed monolayer was recorded during the up and down strokes of the plate. The first layer was deposited on the downstroke, and then the plate was kept in the water for 60 s. After the second layer was deposited on the upstroke, the plate was allowed to dry in the air for 900 s to avoid retransferring of the second monolayer to the water surface. This process was repeated 10 times to obtained LB film with 20 layers for monomers and polymers.



$$\mathrm{RCONHCH_2CH_2{-}\underset{CH_3}{\overset{CH_3}{N^+}}{-}(CH_2)_2{-}O{-}\underset{O^-}{\overset{O}{\overset{\|}{P}}}{-}O{-}(CH_2)_nCH_3}$$

n	11	17	19	21
Monomer R : $CH_2{=}CH{-}$	**1**	**2**	**3**	**4**
Polymer R : $-(CH_2{-}CH)_n-$	**1**	**2**	**3**	**4**

Figure 1. The representative structural formula of amphiphilic monomers and homopolymers.

Contact Angle Measurement

The water contact angles of obtained LB films of the monomers and polymers were measured at room temperature after the films were dried in a desiccator for 24 hours in the presence of silica gel as a drying agent. The quoted values are the average of 10 measurements of each sample taken during 20 s contact with the water droplet, using a face contact angle meter.

RESULTS AND DISCUSSION

The syntheses and characterizations of monomers 2-[2-(acrylamide ethyl)-dimethyl ammonio]ethyl alkyl phosphates and their homopolymers have previously been described in detail [22]. The representative structural formula of these monomers and polymers is shown in Figure 1. These monomers (1–4) and polymers (1–4) having one hydrocarbon chain for one bulky polar head group, show the amphiphilic property. Therefore, their monolayers and LB films could be prepared by the usual method.

Monolayers of the Amphiphilic Monomers and Polymers

The monomers and homopolymers were spread on the water surface from their chlorobenzene/methanol (4:1, v/v) solutions at different temperatures (5, 15, and 25°C). The relationship between surface pressure (P) and occupied area (A) for

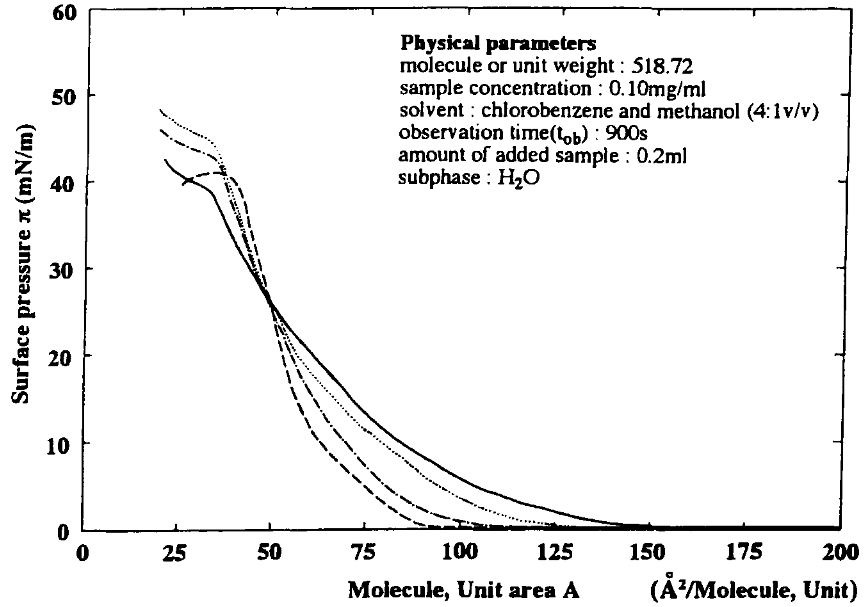


Figure 2. II-A isotherms of monomer **2** at 15°C (——), homopolymer **2** at 5°C (·······), 15°C (·–·–), 25°C (- - -).

a molecule or a polymer unit, as the most basic property of monolayers, was investigated for these monomers and polymers, respectively.

As a result, it has been found that the collapse pressures of homopolymers are higher than those of corresponding monomers at all measured temperatures. This was due to their compacted arrangements of the side chains after polymerizations. The collapse pressures were also found to decrease gradually as the temperature increased for all monomers and polymers. This indicates that the stability of the monolayers increases with the temperature decrease. In addition, the temperature dependence of the monomers' monolayers was observed more readily than that of the polymers' monolayers. It may be due to the stable arrangement of hydrophobic groups of these polymers, in which the amphiphilic side chains are pinned by the main chains at one end.

As an example, Figure 2 illustrates the P-A isotherms of monomer **2** at 15°C and homopolymer **2** at 5, 15, and 25°C, resulting in the formation of stable monolayers. In all experiments, no surface pressure was measurable when the occupied area per molecule or unit is higher than 150 Å². Upon further compression, a monotonic increasing of surface pressure was observed on all isotherms. The isotherms of polymer **2** at different temperatures look similar, except in the collapse range. There is an obvious collapsed point for 5 or 15°C but a collapsed range for 25°C, perhaps due to different collapse mechanisms [23]. The collapse pressures of homopolymer **2** are found to be 48.0, 45.6, and 41.2 mN/m for 5, 15, and 25°C, respectively. Furthermore, the initial rising at 5°C for polymer **2** is earlier than the curves measured at 15°C or 25°C. This may be a result of the poor movability at a low temperature. At the same temperature (15°C), the monomer **2** shows an earlier initial rising of surface pressure, a lower collapse pressure, and a larger occupied area at the collapse point than its homopolymer. These results suggest that the arrangement of hydrocarbon chains on the surface of water is more compacted for the polymer **2** than that for the monomer **2**. Therefore, the formed monolayer is more stable for the polymer either in the ranges of high surface pressure or low surface pressure.

The length dependence of hydrocarbon chains was investigated by measuring the P-A isotherms of the homopolymers **1–4**. The isotherms of polymers **2–4** bearing longer alkyl chains, indicate that these polymers are able to self-organize into densely packed monolayers in the temperature range of 5–25°C. Comparing the curves of the four polymers measured at 15°C (Figure 3), it can be seen that the collapse pressure increases with the increasing of the length of the alkyl group in the side chain since the interaction among the hydrocarbon chains is stronger for longer chains than that for shorter chains. Furthermore, abnormal initial rising and collapsed behavior of the P-A isotherms was observed for homopolymer **1** in comparison with the other polymers. This may be due to the micro-solubility in water for polymer **1** bearing a shorter alkyl chain contrast to the large hydrophilic group in water.

Langmuir-Blodgett (LB) Films of Monomers and Polymers

Currently, there is a growing interest in using performed polymers for the creation of LB films since they are expected to combine increased thermal and mechanical stability with a low defect density [24] as compared to multilayers obained by monomeric amphiphiles polymerization after deposition. However, some performed polymer, such as polyacrylates [25] and polymethacrylates [25] containing relatively weak hydrophilic groups and the preparation of ordered LB multilayers is not always easy [25, 26]. For our approach, the balance of hydrophilic and hydrophilic groups in a polymer is an important factor to prepare a fine LB film. Therefore, in this study, the synthesized amphiphilic monomers and

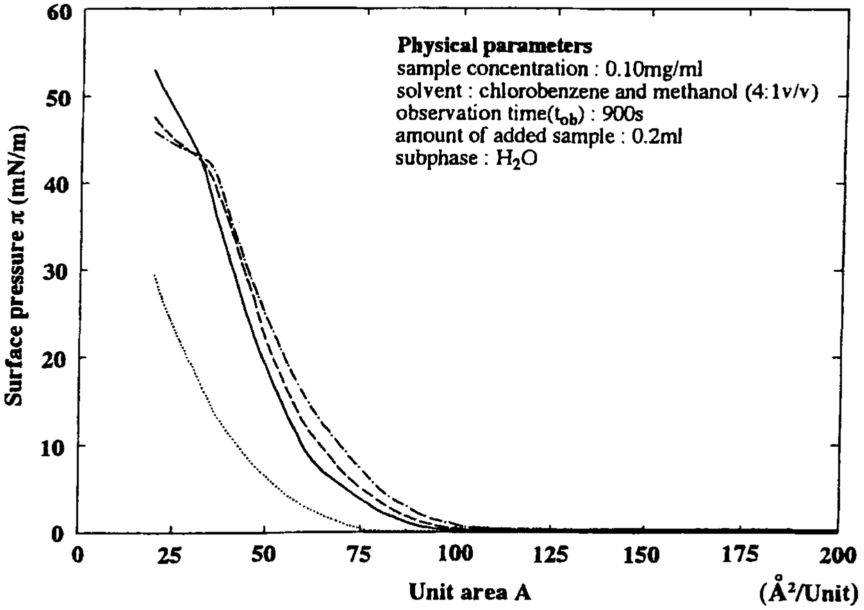


Figure 3. II-A isotherms of homopolymers **1** (·······); **2** (-·-); **3** (- - -); **4** (——) at 15°C.

polymers bearing relatively strong hydrophilic phosphatidylcholine analogous groups and acrylamidic groups in the polar heads were used to prepare Y-type LB multilayers. Furthermore, differing from usual methods in the investigation of LB films such as electron diffraction and small angle X-ray scattering experiments [4, 5, 7], we discussed the properties of these multilayers based on their deposition ratios and investigated the hydrophobicity-hydrophilicity of the surface of the LB films obtained by measuring the contact angles with water.

The monolayer of monomer **1** on the water surface could be transferred onto a hydrophobic wafer PET plate for only four layers at a surface pressure of 15 mN/m, using the vertical dipping method. The deposition ratios (deposited area/ dipped area of plate) were obtained by recording the amount of the films consumed during the successive up and down strokes of the plate. The odd layers were deposited on the downstrokes, and the even layers were deposited on the upstrokes. The averaged deposition ratio was 0.53 of the two downstroking processes in which the monolayer could be adsorbed onto the PET wafer from the part of hydrophobic groups, while it was 0.94 for the even layers that deposited by the interaction of hydrophilic groups. These results indicated that the hydrophilicity of monomer **1** is stronger than the hydrophobicity, not giving a good Y-type multilayer.

The monomers **2-4**, having longer hydrocarbon chains, were transferred for 8-10 layers at a surface pressure of 30 mN/m. The averaged deposition ratio on the down-strokes was 0.64 for monomer **2**, 0.70 for monomer **3**, and 0.73 for monomer **4**, while it was 1.0 ± 0.05 on the upstrokes for the three monomers. From these experiments, the hydrophobicity was found to increase with the rising of the length of alkyl chains, forming better Y-type multilayers. However, from the deposition ratios on up- and down-strokes, it can be concluded that the hydrophobicity is still weak comparing with the hydrophilicity even for monomer **4** containing the longest alkyl chain.

On the other hand, the homopolymers **1-4** were transferred onto PET plates at a surface pressure as well as their monomers. The distinct improvement is that all polymers could be transferred for 20 layers although the averaged deposition ratio of homopolymer **1** on the downstrokes (0.68) was still lower than that on the upstrokes (0.99). Furthermore, the homopolymers show higher deposition ratios on the downstrokes and show similar deposition ratios on the upstrokes, comparing with their corresponding monomers. This may be due to the increased hydrophobicity after introduced hydrophobic main chains, and the excellent mechanical stability of LB films obtained from performed polymers.

As shown in Figure 4, the deposition ratios for homopolymer **2** and **4** were plotted against the number of up and down movements of the plates. Although homopolymer **2** deposited well on the upstrokes (deposition ratios 1.00 ± 0.05), depositions were not perfect on the downstrokes (deposition ratios 0.71 ~ 0.95). While the homopolymer **4** deposited well both on the downstrokes and upstrokes to give a good Y-type film (deposition ratios 0.90 ± 0.05 for odd layers and 1.00 ± 0.05 even layers). From these results, it could be clearly seen that the balance of hydrophobicity and hydrophilicity for homopolymer **4**, having the longest alkyl group in the side chain, is excellent in preparing a good Y-type LB film.

Contact Angles of LB Films

The water contact angle is a common evaluator to the hydrophilicity-hydrophobicity of the film materials surface. After the LB films (four layers) were dried, the water contact angles with obtained LB films for monomers and polymers were measured at room temperature. The results were summarized in Table 1. The contact angles were found to increase with the growth of hydrocarbon chains' length for all the monomers and polymers. Furthermore, they are larger for homopolymers than their corresponding monomers due to the highly compacted assembly of the

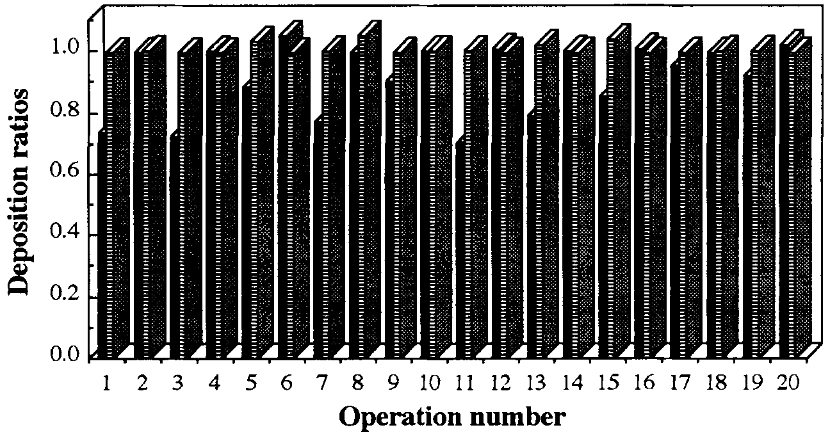


Figure 4. Deposition ratios of LB Films of homopolymer **2** (■) and homopolymer **4** (▤).

TABLE 1. The Contact Angles of LB Films with Water

Monomers and Polymers	Contact Angles (°)	Number of Layers	Layers Type
Monomer **1**	50.5	4	Y
Monomer **2**	57.2	4	Y
Monomer **3**	58.5	4	Y
Monomer **4**	64.8	4	Y
homopolymer **1**	71.6	4	Y
homopolymer **2**	80.3	4	Y
homopolymer **3**	84.0	4	Y
homopolymer **4**	87.5	4	Y

alkyl chains. It is also suggested that the arrangements of obtained LB film for homopolymers are more orderly than those of the monomers since the amphiphilic side chains are pinned by their main chains at one end.

CONCLUSION

The monolayers of some amphiphilic phospholipid analogous acrylamide monomers and homopolymers, having both long alkyl groups and phosphatidylcholine analogues, were prepared on the water surface and their P-A isotherms were investigated at different temperatures, respectively. The collapse pressures of these P-A isotherms were found to decrease gradually as the temperature increased for all monomers and polymers, and they are higher for homopolymers than those of the corresponding monomers. It was also revealed that the collapse pressure increases with the increasing of the length of alkyl group in the side chains. In addition, the LB multilayers of all monomers and polymers were prepared by transferring their monolayers onto PET plates, and the well Y-type LB film was obtained for the homopolymer 4 which contains the longest alkyl chain as the hydrophobic group. Furthermore, the results of water contact angle measurements for the obtained LB films of the monomers and polymers also suggest that the arrangements of alkyl groups are more orderly for the polymers than those for the monomers.

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