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Monolayers of Poly(α,β-aspartic acid) with Long Alkyl Chains and Miscibility with L-α-Phosphatidylcholine at Air-Water Interface

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ABSTRACT
Surface pressure/area isotherms of polypeptides modified with long alkyl chains and their miscibility with DPPC were investigated. The modified polypeptides formed stable monolayers due to their hairy-rod structure and limiting area increased as the degree of substitution increased. Collapse pressure of mixed monolayers deviated from ideal mixture and the free energies of mixing were negative values in all composition.

Keywords air-water interface; monolayer; poly(α,β-aspartic acid); DPPC; miscibility

INTRODUCTION

Many approaches to modify polypeptides have been performed to elucidate conformational change of polypeptides[1]. Particularly, Langmuir-Blodgett films of modified polypeptides have been extensively studied because modified polypeptides are composed of rigid-rodlike backbone and flexible side chains that can form a stable monolayer by forming "hairy-rod"[2,3].

In this study, poly(α,β-aspartic acid) (PAsp) was used for a model of polypeptide, and long alkyl groups were covalently grafted to this model polypeptide. For investigating the interaction of the graft polypeptides and biological membranes, dipalmitoyl L-α-phosphatidylcholine (DPPC) was selected as a model phospholipid and its miscibility with the graft polypeptides was studied.

EXPERIMENTAL

Synthetic scheme of poly(succinimide) (PSI) with or without alkyl groups was described in detail in our previous paper[4]. Synthesized PSI was dissolved with alkylamine in DMF and stirred at 60°C for 24h. When the remaining succinimide unit of PSI is hydrolyzed by NaOH, the resulting polypeptide is PAsp-Cn(n=12 or 18), and it is PAsn-Cn in the case of hydrolysis by ammonium hydroxide. Degree of substitution (DS) was defined as the ratio of the grafting unit to the total succinimide unit. The π–A isotherms were measured by using KSV 5000 Langmuir-Blodgett system, equipped with Wilhelmy plate. The monolayer structure was directly visualized by Brewster angle microscopy (BAM).

RESULT AND DISCUSSION

Synthesized PAsp and PAsn without long alkyl chains showed poor π - A isotherms because of the dissolution into subphase. However, PAsn modified with long alkyl chains formed a stable monolayer because

modified polypeptides make hairy-rod structure like Figure 1-a. Degree of substitution was calculated by ^{1}H-NMR(DMSO-*d6*) and limiting areas of PAsn-C12 with different DS were shown in Table 1.

TABLE 1. Monolayer properties of PAsn-C12

	PAsn-C12				
DS [%]	20	26.1	50	75	100
^{1}H-NMR [%]	19	23.2	49.6	72.2	-*
Limiting area [A^2/repeat unit]	1.4	1.8	4.7	13.1	18.1

* Not determined because of insolubility in DMSO-*d6*

On compression of the monolayer of PAsn-C12, the domain formation was observed in initial stage by BAM, however, domains disappeared after transition to a steeply sloping linear region because homogeneous monolayer was formed by the close packing of encountered domains.

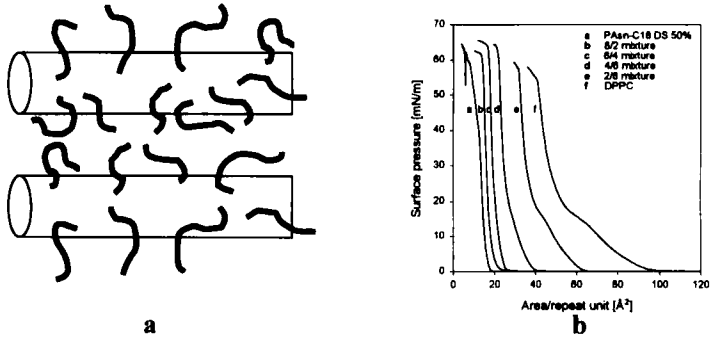

FIGURE 1. **a** Hairy-rod structure of modified polypeptides **b** π-A isotherms of PAsn-C18 (DS=50%) and DPPC mixture

Two-dimensional miscibility of the mixture of DPPC and PAsn-C18 (DS=50%) were investigated by isotherm behaviors. Figure 1-b shows π-A isotherms of the mixture. Though each component has different

collapse pressures, the isotherms of mixtures show only a single different collapse pressure as shown in Figure 2-a.

As suggested by other study[5], the excess free energy of mixing at a given surface pressure was calculated to provide a more quantitative description of the mixing of PAsn-C18 and DPPC in the monolayer. Excess free energies at π=50 mN/m show more negative deviation from ideality than those at π=10 mN/m as shown in Figure 2-b. Therefore, the free energies for mixed monolayer give distinct negative values. This result indicates that PAsn-C18 and DPPC have a thermodynamic miscibility in monolayer system throughout the composition.

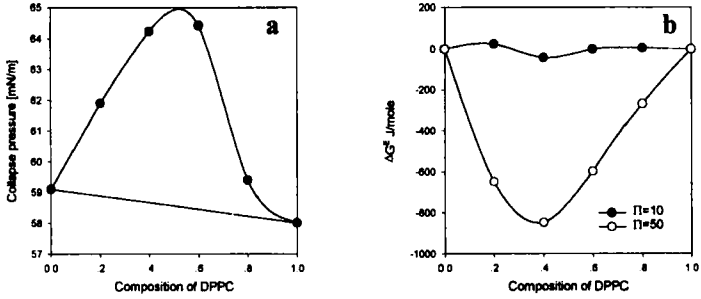

FIGURE 2. **a** Collapse pressure against DPPC composition **b** Excess free energy of mixing vs DPPC composition at surface pressure 10 and 50 mN/m

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