Synthesis and Polymerization of the 16-(Methacryloyloxy)-Hexadecanoic Acid and Phospholipid in Monolayers

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ABSTRACT: Two surface-active monomers with methacrylic group at the end of hydrophobic tail : 16-(methacryloyloxy)hexadecanoic acid (16-MAHDA) and bis[16-(methacryloyloxy)hexadecanoil]-phosphatidylcholine (16-MAHDPC) have been synthesized and investigated. The monomers form stable monolayers at the liquid/gas interfaces with liquid-expanded and liquid-condensed states at low and high surface pressures, respectively. These monomers have been polymerized in the monolayers by low intensity UV-irradiation (254 nm). Dependences of polymerization rate vs. surface pressure for both monomers have maxima ($3.4 \cdot 10^{-4}$ s^{-1} for 16-MAHDA and $5.5 \cdot 10^{-4}$ s^{-1} for 16-MAHDPC) at about 12 mN/m. The higher rate of 16-MAHDPC polymerization as compared to 16-MAHDA is due to the two polymerizable group in the molecule of lipid as compared to the only one in the molecule of acid. The collapse pressures increase after monomer polymerization that evidences an increase of the monolayer stability in the case of polymer as compared to monomer.

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Introduction

Ultrathin polymeric oriented membranes are promising materials for advanced nanotechnology and also can serve as model systems for investigation of biological membranes [1-3]. The polymerization of surface-active monomers in monolayers at the gas/liquid interfaces is the unique method for preparation of some of these membranes. The structure of the obtained polymeric layers depends strongly on the nature and position of the polymerizable groups in the surface-active monomers (SAM), for example, in hydrophilic or hydrophobic part of the molecule [1, 3, 4]. There are some publications [4-10] concerning synthesis and polymerization in monolayers at the air/water interfaces of the surface-active monomers with acrylic or methacrylic group in the hydrophilic "head" of the molecule. The fundamental studies of octadecylmethacrylate (ODMA) and octadecylacrylate (ODA) polymerization in monolayers at different conditions were performed by H. Ringsdorf *et.al.* [4-8]. It was shown a better monolayer characteristics of the polymers prepared directly by SAM polymerization at the liquid/gas interfaces as compared to the preformed polymers in bulk, probably, because of the higher stereoregularity [5]. It is especially pronounced in the case of ODMA polymerization in monolayers, which allows a better packing due to a side chain crystallization under compression, as compared to the "bulk" polymer [6]. The first attempt in studing polymerization kinetics in monolayers was described also in the work of H. Ringsdorf *et.al.* [5] on the example of ODA monolayers. The further development in the field of various SAM polymerization in monolayers, especially kinetics studies, was fulfilled in our works [3, 9-12].

The few recent publications in this field of T. Miyashita et al. [13] and F. Caruso et al. [14] are devoted to ODA and ODMA polymerization in monolayers at the air/water interfaces in the mixture with other surface-active monomers, in order to investigate their reactivity [13], or chromophores, which allows to study their lateral diffusion at the interface [14]. The main studies of the monolayers of acrylic or methacrylic polymers preformed in "bulk" are discussed in the fundamental rewiev of V. Arslanov [2]. One example of the recent studies of the surface-active and viscoelastic properties of polymethylmethacrylate monolayers with different molar masses is shown in the publication of G.T.Barnes *et al.* [15].

The complete description of synthesis of the unique lipid-like monomer: bis[12-(methacryloyloxy)dodecanoyl]-phosphatidylcholine, having methacrylic groups at the end of the hydrophobic tails was made by S.L. Regen *et.al.* [16]. But the polymerization of this monomer was studied only in liposomes [16]. Based on this pioneer study, we synthesized similar SAM and studied its polymerization in monolayers [17]. But, hydrophobicity of this monomer was not sufficient for preparation of a stable monolayers at the water/air interface at high surface pressures [17] and we decided to prepare a monomer with longer hydrocarbon chain.

This work is devoted to the synthesis and polymerization in monolayers at the air/water interfaces of the surface-active monomers such as 16-(methacryloyloxy)-hexadecanoic acid (16-MAHDA) and bis[16-(methacryloyloxy)hexadecanoyl]-phosphatidylcholine (16-MAHDPC) with methacrylic group at the end of the hydrophobic tail.

Experimental

16-(methacryloyloxy)hexadecanoic acid and bis[16-(methacryloyloxy)-hexadecanoyl]-phosphatidylcholine were prepared according to the described methods [16] with small modifications [17] (Scheme).

Monolayers of surface-active monomers have been prepared and studied on a commercial film balance ("Lauda", FRG). The samples of the monomers (10 μl from 10 mM solutions) have been spread onto 1.0 mM phosphate buffer subphases pH 7.0, 20°C between moving and measuring barriers. The prepared monolayers have been compressed by moving barrier with constant speed of about 1 cm^2/s and the isotherms of surface pressure (π) vs. area (A) of the monolayer have been recorded.

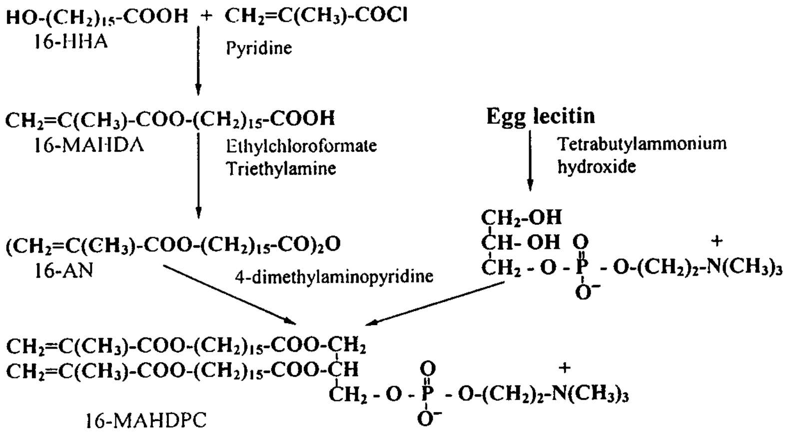
Polymerization of the lipid-like monomers in monolayers has been initiated by soft UV- irradiation (λ 254 nm, 10 mW/cm^2) without organic initiators in the inert atmosphere. The kinetics of polymerization has been measured as contractions of monolayer area during UV-irradiation at some selected constant pressures. The rate of polymerization (V) has been calculated according to the equation:

$$V = (\Delta h_t / \Delta h_{max.}) / t ,$$

where Δh_t - contraction of the monolayer at the time (t) of UV-irradiation; $\Delta h_{max.}$ - maximum contraction of the monolayer at the end of polymerization. The preparation of the polymer has been additionally controlled by the spectroscopic measurements of the multilayer films, transferred after UV-irradiation onto quartz plates.

Results and Discussion

It has been shown that all synthesized monomers and the initial hydoxycarbonic fatty acid, form monolayers at the liquid/gas interfaces. There are two regions with different slopes on the surface pressure (π) - area per molecule (A) isotherm for 16-MAHDA, which can be assigned to the two states of monolayer: liquid-expanded state I (at p below 14 mN/m) and liquid-condensed state II (π in the range of 16-24 mN/m), respectively (Fig. 1, curve 1). The area per molecule in state I extrapolated to zero surface pressure is about 1.20 nm^2, that is close to the dimentions of the hydrophobic tail of 16-MAHDA, if it is oriented parallel to the liquid/gas interface. The extrapolated area in state II is about 0.52 nm^2, that is much lower than those in state I, but higher than the cross-section of the hydrophobic tail of the acid, if it is oriented perpendicular to the liquid/gas interface. Probably, SAM



Scheme of synthesis SAM

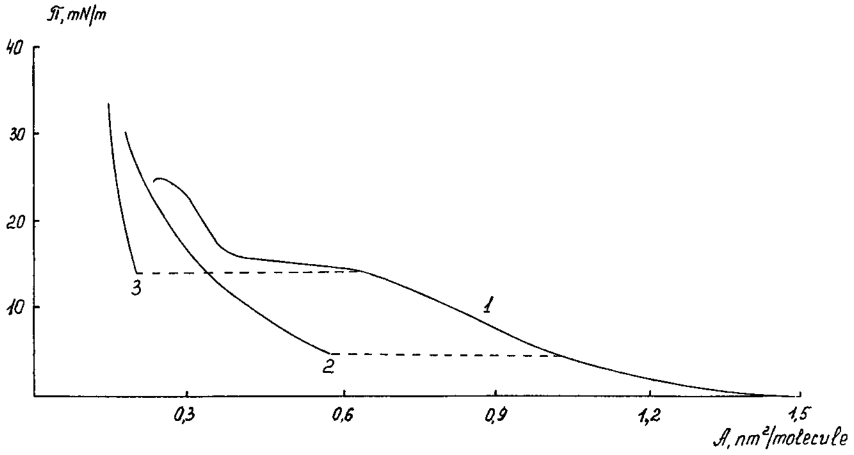


Fig. 1. Surface pressure (π) - molecular area (A) isotherms for monolayers of 16-MAHDA monomer (1) and polymers (2, 3), obtained by UV-irradiation (254 nm) at 5 mN/m (2) and 14 mN/m (3).

molecules in state II are oriented with some tilt to the interfaces. Thus, the sharp transition (in the form of plateau on π-A isotherms) between two states for 16-MAHDA monolayers can be assigned to the reorientation of the hydrophobic tail of 16-MAHDA from parallel to vertical (with some tilt) as referred to the liquid/gas interface. That is in agreement with the previous works [17, 18].

The transition between liquid-expanded and liquid-condensed states for 16-MAHDPC monolayers (Fig. 2, curve 1) occurs at the same values of surface pressures, but is not so pronounced as compared to 16-MAHDA (Fig. 1, curve 1). The collapse of the lipid monolayer has been observed at surface pressure about 34 mN/m (Fig. 2) that is much higher as 25 mN/m for the 16-MAHDA monolayers (Fig. 1). These differences between fatty acid and lipid can be explained by the primary influence of the large hydrophilic "head", as compared to the hydrophobic tail, on the monolayer properties of 16-MAHDPC. The collapse areas per 16-MAHDA and 16-MAHDPC are almost similar in the range of 0.28-0.32 nm^2/molecule, that is higher than those for the initial hydroxycarbonic fatty acid. Thus, an introduction of the methacrylic group in the acid or lipid molecules leads to the more expanded monolayer films as compared to the initial hydroxycarbonic fatty acid.

These monomers have been polymerized in monolayer at the liquid/gas interface by soft UV-irradiation (254 nm) without radical initiators in order to simplify a kinetic picture. As was shown earlier for various SAM [1, 3, 4], a decrease in the area during UV-irradiation of SAM monolayers is proportional to the contraction of monomer to polymer. Such method to study the rates of SAM polymerization in monolayers can be considered as two-dimentional dilatometry. Areas per monomer unit in the obtained polymeric monolayers are much smaller then those for the monomer one and correlate with the monomer contraction in the volume during polymerization. The absolute values of these areas decrease with increasing surface pressure at which the polymerization takes place (Figs. 1, 2). The collapse pressures

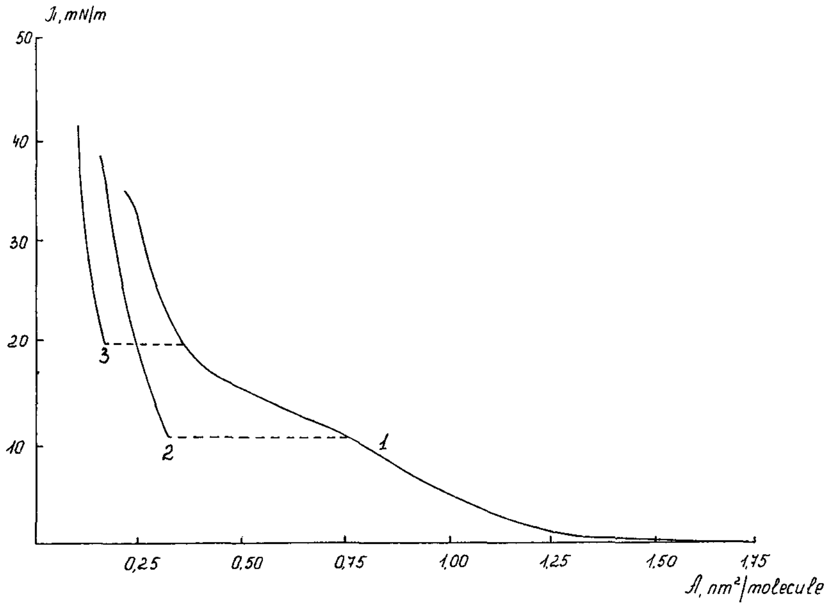


Fig. 2. Surface pressure (π) - molecular area (A) isotherms for monolayers of 16-MAHDPC monomer (1) and polymers (2, 3), obtained by UV-irradiation (254 nm) at 10 mN/m (2) and 20 mN/m (3).

increase after polymerization for both monomers that evidences the increase of the monolayer stability in case of polymer as compared to monomer.

The rates of polymerization for both monomers (Fig. 3) increase drastically with small increase in the surface pressure that correlates with the increase in orientation of the SAM in the liquid-expanded state I of the monolayer. Dependences of polymerization rate vs. surface pressure have maxima at π about 12 mN/m for both monomers (Fig. 3) that is close to the transition point between two states in

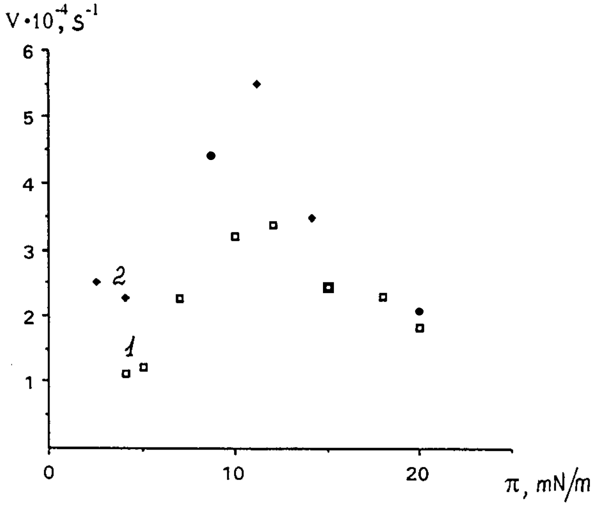


Fig. 3. Rates of polymerization (V) vs. surface pressure (π) for 16-MAHDA (1) and 16-MAHDPC (2) in monolayers.

monolayer (liquid-expanded and liquid-condensed) on the surface pressure - molecular area isotherms (Figs. 1, 2). Maximal polymerization rate of 16-MAHDPC ($5.5*10^{-4}$ s^{-1}) is higher than those of 16-MAHDA ($3.4*10^{-4}$ s^{-1}) that is, probably, due to the more dense packing of lipid molecules in monolayer as compared to the acid. After pronounced maxima at 12 mN/m the rates of polymerization sharply decrease with further increase of surface pressure until monolayer collapse. Such decrease in the rate of polymerization for both monomers can be explained by sterical difficulties in the interaction between polymerizable groups in the highly compressed monolayers, especially close to the collapse points. The found dependences of polymerization rate vs. surface pressure (e.g. degree of monomer orienation) for 16-MAHDA and 16-MAHDPC in monolayers with pronounced maxima at middle π values are in agreement with the general dependences for the SAM having acrylic and methacrylic groups in the hydrophilic part of the molecules [5, 10, 12].

Thus, surface active monomers with methacrylic group at the end of hydrocarbon tail were synthesized and their monolayers at the liquid/gas interfaces were prepared. The peculiarities of kinetics of SAM polymerization in monolayers can be explained by changes in orientation of the monomer molecules at the interfaces. According to their properties, these SAM can be used for immobilization of various biologically active substances, as model systems for investigation of biological membranes and also as promising materials for advanced nanotechnology.

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