

The behavior of fatty acid modified poly(glycerol adipate) at the air/water interface



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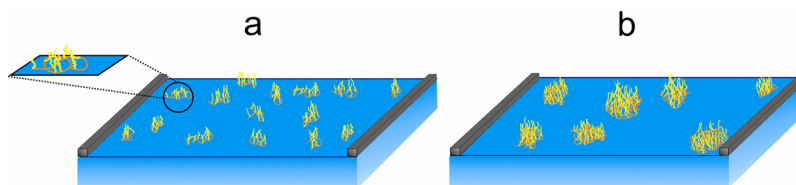
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HIGHLIGHTS

- The surface behavior of poly(glycerol adipate) (PGA) significantly changes after grafting fatty acids to the PGA backbone.
- For higher substitution ratio the monolayer tends to destabilize.
- The length of the grafted acyl chains significantly influences the stability and compressibility of the monolayer.

GRAPHICAL ABSTRACT

The influence of hydrophobic modification with fatty acids of various chain lengths on the behavior of poly(glycerol adipate) at the air/water interface is investigated. With increasing length of the grafted acyl chains the stability and compressibility of the film on the water surface increases because of enhanced coherence between the alkyl side chains.



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ABSTRACT

The influence of hydrophobic modification with fatty acids of various lengths on the behavior of poly(glycerol adipate) (PGA) at the air/water interface is investigated. The Langmuir isotherm of unmodified PGA reveals a liquid expanded (LE) phase followed by film collapse as indicated by the plateau starting at π_c (collapse pressure) ~ 13 mN/m. The film stability increases significantly by grafting fatty acids to the PGA backbone; PGA-*graft*-acyl. However, it tends to decrease again for higher degree of substitution due to the decreasing number of pendant hydroxyl groups on PGA backbone, which stabilize the monolayer by forming hydrogen bonds with water molecules. For samples with higher degree of substitutions, the LE phase could not be detected in the Langmuir isotherm which only shows a sharp increase in surface pressure, corresponding to the liquid condensed (LC) phase, followed by the film collapse. Atomic force microscopy images of the Langmuir–Blodgett films depict the formation of 3D nuclei of different heights at surface pressure, $\pi > \pi_c$ and the Brewster angle microscopy images reveal the formation of buckles in the collapse region for PGA-*graft*-tridecyl films. The formation of a solid phase in the Langmuir film is observed only for PGA grafted with longer alkyl side chains, including, heptadecyl and heneicosanyl. Overall, it is observed that with increasing length of the acyl chains the stability and compressibility of the film on the water surface increases because of enhanced coherence between the alkyl side chains that overcomes the obstruction effect of the PGA backbone.

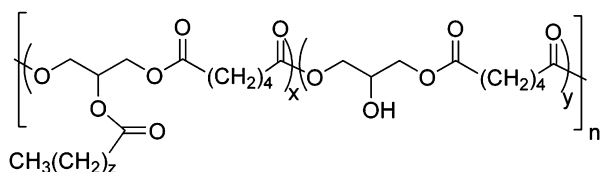
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1. Introduction

The self-assembly of amphiphilic molecules at the air/water interface can be studied by measuring the surface pressure, π as a function of mean molecular area (*mmA*) using a Langmuir

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Scheme 1. Chemical structure of PGA-graft-acyl.

trough [1]. In most cases, Langmuir trough is equipped with other tools, such as Brewster-angle microscope (BAM) [2], infrared reflection-absorption spectroscopy [3,4], fluorescence microscopy (FM) [5], and X-ray and neutron reflectometry [6] to get molecular level information during compression of the film on the water surface. Although, the Langmuir-Blodgett (LB) technique (the transfer of films deposited on the water surface onto a solid support) is about eight decades old [7], yet it is still considered as the key technique for the preparation of thin films with huge potential in areas, such as biosensors [8–11], molecular electronics [1], hard nanomaterials [12], nanocrystals and nanowires [13,14].

Amphiphilic comb-like copolymers based on various functional polymers as the backbone such as cellulose [15–26], poly(L-glutamate) [27,28], poly(*N*-acylethylenimines) [29,30], poly(phenylene ethynylene) [31,32], poly(maleic acid) [33], polythiophene [34], poly(vinyl pyridine) [35,36], and poly(vinyl alcohol) [37] have been extensively investigated at the air/water interface. Previously, our group reported the behavior of poly(glycerol adipate) (PGA)-graft-poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) and PGA-graft-poly(ϵ -caprolactone) in solution [38] as well as at the air/water interface [39], where the crystallization of grafted poly(ϵ -caprolactone) (PCL) was observed and compared with that of linear PCL on water surface. In the current study we intend to explore and understand the behavior of poly(glycerol adipate) (PGA) and its hydrophobically modified derivatives, achieved via grafting with *n*-acyl side chains of various lengths. PGA, a biodegradable and biocompatible polyester, equipped with pendant OH group in each repeat unit (Scheme 1), is synthesized enzymatically from cheap and commercially available monomers, namely, glycerol and divinyl adipate [40,41]. The OH groups at the PGA backbone can be esterified by treating with fatty acid chloride using standard protocols [42] to achieve the hydrophobically modified PAG derivatives (PGA-graft-acyl).

Previous investigations on PGA-graft-acyl have shown well-defined nanophase separation between the polyester backbone and the *n*-acyl side chains and depending on the degree of esterification of the pendant OH groups of PGA backbone, resulted into nanostructured nanoparticles with various morphologies from nanoemulsions [43]. For instance, at high degree of esterification, the formation of a perfect lamellar morphology within the spherical nanoparticles was observed, while at lower degree of esterification (20 mol%), polygonal nanoparticles with an internal pseudo-hexagonal structures were obtained. Because of their biodegradability, non-toxicity [44], these materials have received attention for applications in the field of nanoparticulate drug delivery systems [42,43,45,46].

Herein, our aim is to investigate the structure–property relationship between the structure of amphiphilic comb-like PGA-graft-acyl, i.e. degree of substitution and length of the *n*-acyl side chains, and its molecular arrangement at the air/water interface. Thus, we present a systematic study on the interfacial properties of PGA-graft-acyl, with various molar masses of PGA, various degrees of substitutions by different aliphatic acyl chains, including, undecyl, tridecyl, heptadecyl, and hencicosanyl by measuring the Langmuir isotherm, Brewster angle microscopy, and atomic force microscopy of the LB film transferred onto silicon substrates.

2. Experimental

2.1. Materials

The synthesis of poly(glycerol adipate) (PGA) and esterification of its pendant OH groups via treatment with various aliphatic acid chlorides to achieve PGA-graft-acyl was carried out as reported elsewhere [42,47]. The samples are named as: PGA_x-graft-acyl_y, where the subscripts 'x' and 'y' represent, respectively, the molar mass (M_n) of the PGA backbone in g/mol obtained by size exclusion chromatography, and the mol% substitution of the available OH groups on the PGA backbone, obtained by ¹H NMR spectroscopy. The polydispersity (M_w/M_n) of all polymer backbones is approximately 2. The common chemical structure of PGA-graft-acyl is depicted in Scheme 1.

The following samples were included in our study: PGA₃₅₀₀, PGA₃₅₀₀-graft-undecyl₈, PGA₃₅₀₀-graft-undecyl₂₄, PGA₃₅₀₀-graft-undecyl₅₆, PGA₂₀₀₀, PGA₂₀₀₀-graft-tridecyl₁₅, PGA₂₀₀₀-graft-tridecyl₁₀₀, PGA₃₇₀₀, PGA₃₇₀₀-graft-heptadecyl₂₀, PGA₃₇₀₀-graft-heptadecyl₅₀, PGA₃₇₀₀-graft-heptadecyl₆₅, PGA₃₇₀₀-graft-hencicosanyl₄₅. The length of the grafted chain in term of number of carbon atoms, excluding the carbonyl carbon, is C₁₀, C₁₂, C₁₆, and C₂₀ in PGA-graft-undecyl, PGA-graft-tridecyl, PGA-graft-heptadecyl, PGA-graft-hencicosanyl, respectively.

2.2. Surface pressure measurements

The surface pressure, π as a function of mean molecular area (mm^2) was measured using a Langmuir trough system (KSV, Helsinki, Finland) equipped with a micro-roughened platinum Wilhelmy plate. The temperature of the water subphase was adjusted by a circulating water bath system. All experiments were carried out at 20 °C unless otherwise stated. The compression and expansion rate for all experiments was 750 mm²/min. The water employed as subphase was purified deionized water (TKA Gen-Pure Labor&Reinstwassertechnik Christian Wiesenack, Jena) with a conductivity <0.056 μ S/cm. The polymer solutions with HPLC grade chloroform were spread on the subphase using a digital microsyringe (Hamilton). The chloroform was allowed to evaporate for 20 min before compression of the film started. The polymer solutions were spread at different initial surface pressures, and different parts of the isotherm were recorded in order to obtain the complete isotherms. Thus, different regions of the isotherm were first recorded and later combined to produce a complete isotherm.

2.3. Brewster angle microscopy (BAM)

Direct observation of the films formed by different PGA-graft-acyl samples at air/water interface was carried out using a MiniBAM instrument (Nanofilm Technologie GmbH, Germany) delivering images from a surface of around 7 × 5 mm² with a lateral resolution of approximately 20 μ m.

2.4. Langmuir-Blodgett (LB) films

The deposition of polymer films formed at air/water interface was carried out on hydrophobically modified silicon wafer. For this purpose, the surface of silicon wafer was hydrophobically modified according to the procedure described by Peetla et al. [48] After treatment, the silicon substrates were then cut into small pieces (1 cm × 1.5 cm) and immersed into the water subphase of the Langmuir trough. The polymer solution was then spread onto the water surface and after 20 min of waiting; the surface was compressed using a compression rate of 750 mm²/min until the desired transfer surface pressure was achieved. After waiting for 20 min at the desired surface pressure, the film was then transferred onto the

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