



# Phase transitions in monolayer formed by hyperbranched polyester with alkyl-terminated branches at the air/water interface

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## ABSTRACT

Investigations of Langmuir and Langmuir–Blodgett molecular films of hyperbranched polyester with alkyl-terminated branches over a wide temperature range revealed an unusual phase transitions. The measured surface pressure–surface area isotherms clearly show that the hyperbranched polyester formed stable and well-defined monolayers at the air/water interface. At temperatures below 313 K ice floe-like structures of a condensed phase were formed already from very low surface pressures. On the increase of the surface pressure the floes of the condensed phase merged forming a uniform monolayer. Above 313 K a surface liquid phase was formed at the interface. It was shown that the phase transition from the surface liquid phase to the condensed phase occurred on temperature decrease. At lower temperatures the compression process was not reversible. The increase of temperature up to about 323 K made the compression process reversible. The monolayers were transferred from the air/water interface onto silicon and mica substrates using the Langmuir–Blodgett technique at different temperatures. The structure of the polyester monolayer formed at the substrates' surfaces was investigated.

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## 1. Introduction

Molecular films of polymers spread at the air/water interface and their transfer onto solid substrates have been the subject of extensive research for many years. The driving force for research is the possible applications in the fields of optics, biosensors, coatings, microlithography and electronics. Many types of synthetic polymers and biopolymers have been studied as monolayers at the air/water interface and on solid substrates [1–8]. In recent years Langmuir and Langmuir–Blodgett molecular films of amphiphilic dendritic polymers have been also investigated [9–17].

The properties of dendritic polymers are affected by the nature of the backbone, the terminal groups functionality, the degree of branching, the chain length between branching points, and the molecular weight distribution [18]. End-capping of the hydrophilic dendritic macromolecules with hydrophobic alkyl chains makes the modified molecules amphiphilic. It has already been recognized that these macromolecular amphiphiles form well-defined monolayers both at the air/water interface and on solid substrates. Most of the research reported in the literature concern modified

dendrimers of different generations. Sayed-Sweet et al. [9] investigated poly(amidoamine) (PAMAM) dendrimers modified with aliphatic chains with 8, 10 and 12 carbon atoms. The authors showed that the properties of the modified PAMAM dendrimers at the air/water interface strongly depend on dendrimer generation. In their experiments the length of the terminal alkyl chains did not significantly influence the surface area occupied by the dendrimer molecules at the collapse point. The authors also proved that modified dendrimers with guest molecules placed in the interior void space were able to form monolayers at the air/water interface. Schenning et al. [10] investigated poly-(propylene imine) dendrimers modified with palmitoyl chains, alkyl chains containing azobenzene chromophore and adamantane. From Langmuir experiments the authors concluded that the dendrimer molecules were able to arrange themselves into monolayers in which the dendrimer core was in contact with the water subphase and the alkyl terminal chains were all pointing toward the air, forming a parallel-packed hydrophobic layer.

The transfer of the third-generation PAMAM dendrimer end-capped with dodecyl chains onto hydrophobic silicon wafers was investigated by Tanaka et al. [11]. At the beginning the dendrimer molecules were in contact with the surface through alkyl chains. The authors suggested that during the drying process the silicon surface became hydrophilic and at the same time the PAMAM molecules turned upside down. Poly-(propylene imine)

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dendrimer modified with dialkyl sulfide chains investigated by Liebau et al. [12] self-organized into monolayers in the same fashion as dendrimers end-capped with alkyl chains. Investigations of the surface behavior of multidendron structures were also reported in the literature. Saville et al. [13,14] studied the structure and kinetics of surface phase transitions in monolayers formed by polyether bidendrons based on 3,5-dihydroxybenzyl alcohol. The authors also investigated the influence of the molecular weight and compression rate on the shape of Langmuir isotherms. Pao et al. [15] investigated second- and third-generation polyether monodendrons with end groups functionalized with hydrophobic  $C_{12}H_{25}$  alkyl tails and a hydrophilic ester or crown ether in the core. X-ray reflectivity data suggested that at higher surface pressures the alkyl tails were extended and perpendicular to the surface of the water.

The structure of monolayers formed by the amphiphilic dendrimer macromolecules raises the question of the surface behavior of hyperbranched polymers. Are the similarities of dendrimers and hyperbranched polymers big enough for polymers to form supramolecular structures at surfaces and interfaces analogous to dendrimers? Zhai et al. [16] investigated the influence of the degree of hydrophobic substitution of the end groups of second generation hyperbranched polyesters on the behavior at the surfaces and the air/water interface. The polyesters were functionalized with stearic acid. The experiments showed that at high surface pressure, the alkyl tails became arranged in an upright orientation with dense liquid-crystalline like ordering of the quasi-hexagonal type. The authors suggested that in contrast to modified dendrimers irregular branching and random attachments of the terminal alkyl tails in hyperbranched polymers prevented the formation of regular lateral ordering and crystallization of the alkyl tails within Langmuir monolayers. Ornatska et al. [17] investigated the formation of the monolayer at the air/water interface by the hyperbranched polymer Boltorn H40 modified with palmitoyl chloride and the transfer of the monolayer onto the a silicon substrate. The polymer used in the experiments had 80% terminal hydroxyl groups substituted with palmitic acid. As reported by the authors, the modified polyester formed a stable monolayer at the air/water interface. Uniform dense Langmuir–Blodgett monolayers with an effective thickness of 3–4 nm were observed for the polymer molecules transferred onto the solid substrate at different surface pressures.

The current state of knowledge leaves the influence of temperature and the length of the alkyl terminal tail on the surface and interface behavior of modified hyperbranched polymers unknown. In this contribution the surface behavior of polyester with the terminal hydroxyl end groups esterified with a mixture of eicosanoic and docosanoic acid is described. The terminal tails of the polyester are much longer than in other studies reported in the literature. This contribution aims at an understanding of the influence of temperature on the monolayer formation by the modified hyperbranched polyester.

## 2. Experimental section

### 2.1. Materials

Perstorp AB (Sweden) produced a series of hydroxyl-functional hyperbranched polyesters based on 2,2-bis-methylpropionic acid (bis-MPA) with an ethoxylated pentaerythritol core, designated as Boltorn H20, H30, and H40. Boltorn H3200, the hyperbranched polymer used in this work, is synthesized from Boltorn H30 through the esterification of the OH-end groups with a mixture of eicosanoic and docosanoic acid leading to C20/22 alkyl chains as end groups.

### 2.2. Characterization of polymer

The investigated polymer was characterized by means of Nuclear Magnetic Resonance (NMR) spectroscopy and gel permeation chromatography (GPC). For all samples  $^1H$  and  $^{13}C$  spectra were recorded on a Bruker DRX Avance 300 MHz. The spectra of the polymer were measured in  $CD_2Cl_2$  and  $DMSO-d_6$  solutions at 298 K. Gel permeation chromatography (GPC) measurements were performed on an Agilent chromatographic setup coupled to two detectors: a Knauer Refractive Index Detector and a Wyatt Technology DAWN multi-angle laser light scattering (MALLS) detector. A Polymer Laboratories PLGel 5 micron MIXED-C column with a length of 300 mm and inner diameter of 7.5 mm was used. Methylene chloride served as the mobile phase with a flow rate of 0.80 ml/min. The measurements were performed at a temperature of 303 K.

### 2.3. Method and equipment

Experiments were carried out with a Langmuir–Blodgett trough 712BAM/Narrow produced by Nima (UK). The trough was cleaned before each experiment according to standard procedure with the use of solvents of an analytical grade. Ultrapure water (resistivity of 18.2 M $\Omega$  cm) was used as a subphase. The surface pressure was measured using rectangular pieces (20 mm  $\times$  10 mm  $\times$  0.1 mm) of filter paper with a precision of 0.05 mN/m by the Wilhelmy plate method. The temperature was controlled with an accuracy of  $\pm 0.2$  K using a cooling/heating circulation bath (Thermo Scientific, USA) filled with isopropanol/water solution. The temperature was measured with two Pt100 $\Omega$  resistance thermometers immersed at both ends of the trough and connected to a Keithley multimeter. Simultaneous measurements of surface potential (SP) were performed with a vibrating electrode provided by Treck Inc. Brewster Angle Microscopy (BAM) images were taken using MiniBAM (Nanofilm Technology) with a resolution of 8.3  $\mu$ m per pixel. Throughout this paper the scale bars shown in all BAM images correspond to 500  $\mu$ m. The whole system was placed on an active anti-vibration table (Newport) and closed in a Plexiglas<sup>®</sup> box to protect the films against dust and air-currents.

Langmuir experiments were performed using two different strategies (modes) of measurements, i.e. static and dynamic modes. In the dynamic mode 35  $\mu$ l of the polymer chloroform solution (concentration of 1.49 mg/ml) was carefully spread on the surface of water using a microsyringe (Hamilton, USA). The deposition of the polymer was performed at the maximal distance between the barriers, i.e. maximal surface area of the trough. The same volume of the solution was used in all the experiments performed in the dynamic mode. The time delay allowing chloroform to evaporate after applying the polymer solution was always around 15 min. Then the surface area of the trough available to the polymer was reduced by a slow uniform motion of the barriers. Surface pressure ( $\pi$ ) versus surface area ( $A$ ) isotherms were recorded in the dynamic mode with the barriers speed equal to 0.27 nm<sup>2</sup>/molecule/min.

In the static mode the same chloroform solution of the polymer as in the dynamic experiments was used. The static experiments were performed with maximal surface of the trough and the barriers motionless. Portions of the solution of a volume from 2 to 5  $\mu$ l were successively deposited at the air/water interface. After the deposition the system was equilibrated for about 30 min. Then the surface pressure was measured.

The films were transferred onto silicon and mica according to the Langmuir–Blodgett technique with a dipper speed of 10 mm/min. The silicon wafers used for the experiments were provided by the Institute of Electronic Materials Technology (Warsaw, Poland). The wafers were cleaned with acetone, then dipped in nitric acid (30% solution) for 30 min and rinsed several times with water.

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