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Study of the solid–liquid interface of hydroxyl-terminated hyperbranched aromatic polyesters (HBP-OH) in aqueous media I. Characterisation of the properties and swelling behaviour of HBP-OH thin films

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Abstract

The nature of the solid–liquid interface of hydroxyl-terminated hyperbranched aromatic polyester (HPB-OH) thin films has been studied with respect to further protein adsorption investigations. Contact angle measurements, atomic force microscopy, zeta potential measurements and spectroscopic ellipsometry were used to characterize the physical and chemical structure of the HBP-OH thin films as well as the adsorption-relevant surface properties.

It was shown that film properties such as the effective refractive index significantly depends on the thickness of HBP-OH films whereas the water contact angle does not reveal any changes with thickness variations. All surface-sensitive methods used indicate marked swelling behaviour of HBP layers in aqueous phosphate buffer saline. Moreover, the degree of swelling, zeta potential as well as surface free energy (in terms of water contact angle) strongly depend on the time the films had been annealed above their glass transition temperature.

Keywords: Hyperbranched polymers; Swelling; Spectroscopic ellipsometry; Zeta potential; Contact angle measurements

1. Introduction

The attention to hyperbranched polymers (HBP) is rapidly growing due to their unique physical and chemical properties such as low viscosity, high solubility determined by the branching and the high functionality of these macromolecules. Hyperbranched polymers do not have a perfect three-dimensional globular molecular structure. They exhibit a random branched structure including linear, dendritic and terminal units. A large number of reviews concerning the synthesis, modification, and applications of HBP has been published during last years [1–5]. Furthermore, thin films of HBP on solid substrates found a number of technical applications, e.g., as chemical sensors [6,7], diagnostic tools and multifunctional coatings [8–12]. There had been many different methods applied to characterise the properties of the surface of HBP [9,10,13–16]. During the last years polymer films and surfaces in contact with biomolecules are in focus of scientific and technological research activities. This is demonstrated by the increasing number of publications concerning the behaviour, e.g. of complex multilayer systems formed by charged polymers in aqueous solution of different pH, which is the native medium for proteins, cells, enzymes and antibodies. Therefore, it is very important to clarify the dynamic properties of polymer thin films such as swelling, the interaction of polymer molecules with an electrolyte solution with further dissociation or the hydration of polar groups before the interaction with biomolecules can be studied and understood.

The swelling process involves the diffusion of small molecules and ions into existent voids, micro-pores or a free volume of polymers during the dynamic movement. Thus, swelling forces segmental motion within the polymer, resulting in an increased distance between polymer segments. This suggests that the film confinement tends to increase the mobility of small species with further segment relaxation. For example, the transport of ions through polyelectrolyte multilayers has been found to be enhanced with increase of film thickness [17].

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Additionally, McCormick et al. [18] showed that the water absorption of polyelectrolytes increases the polymer mobility when confined in a multilayer system.

The kinetics of the absorption process of small molecules into the polymer matrixes and factors influencing this process have been a field of significant recent attention [19–23]. The influence of the film thickness on the degree of swelling and swelling kinetics of water in thin poly(4-ammonium styrenesulfonic acid) films was examined using X-ray reflectivity and quartz crystal microbalance (QCM) measurements [24]. Ellipsometry was applied to reveal the changes in film thickness of a grafted hyperbranched poly(acrylic acid) as a function of pH [25]. The influence of chemical composition and annealing temperature of phosphorylcholine biocompatible polymer films on swelling mechanism characterised by diffusion and relaxation times was described by Tang et al. [19,20]. The authors also supposed that hydrophilic and hydrophobic fragments of a polymer may promote the formation of a structured morphology within the film which may influenced the water sorption.

In a previous paper [26], the surface properties of thin films of hyperbranched aromatic polyesters terminated by hydroxyl, carboxyl and acetoxy groups were studied. It was found that the surfaces of these polymers are hydrophilic caused by polar functional groups at the outermost surface. Using spectroscopic ellipsometry and reflectometric interference spectroscopy, at first the swelling behaviour of the HBP films was investigated at different atmospheric humidities. From the results it was concluded that these HBP films might be used as sensor materials. Based on the results obtained, HBP were studied in more details. Vapours of a homologous series of alcohols from methanol to pentanol were exposed in the gas phase to the thin films. It was demonstrated that a calibration and discrimination of the analytes is possible depending on the functional groups of the HBP, and the polarity of the analytes, respectively [6]. On the other hand, it was shown that the quantification of an unknown quaternary mixtures of methanol, ethanol, propanol and butanol in aqueous phase is possible using a combination of HBP and polyimide based sensors [7].

Now, HBPs attracted our attention based on the possibility to use them as biocompatible or bioactive materials. Therefore, in the present study, HBP-OH films have been investigated first using different surface-sensitive techniques with respect to further investigations of protein adsorption in an aqueous solution of phosphate buffer saline. Morphology, thickness, and refractive index were checked by scanning force microscopy and spectroscopic ellipsometry. The surface properties of HBP-OH controlled by the nature of terminal groups were determined by water contact angle and zeta potential measurements in aqueous solutions of different pH. The swelling behaviour of the films in the aqueous phase was monitored in situ by spectroscopic ellipsometry and zeta potential measurements.

2. Materials and methods

2.1. 2.1. Materials

The hydroxyl terminated hyperbranched aromatic polyester (HBP-OH) was synthesized by melt polycondensation of 3,5-bis(trimethylsiloxyl)benzoyl chloride and subsequent hydrolysis of silyl ether and acid chloride groups as described previously [27,28]. Its molecular structure is schematically shown in Fig. 1. Proton signals in the aromatic region were found by ^{1}H NMR between 7 and 9 ppm confirming expected chemical composition and branching structure of the compound which is in accordance with literature data [27] and allows to calculate the content of remaining trimethylsiloxy groups, which can affect the surface properties of films, to be only 0.3 mol%. A degree of branching of 0.6 was calculated from the ^{13}C NMR spectrum [27]. Furthermore, a molecular weight M_w of 45.500 g/mol and M_n of 12.600 g/mol was determined by GPC (Agilent HP 1100, Germany) in DMA (Fluka) using PVP (PSS) as standard. The glass transition temperature T_g of the used HBP-OH is 227 °C (DSC 7,

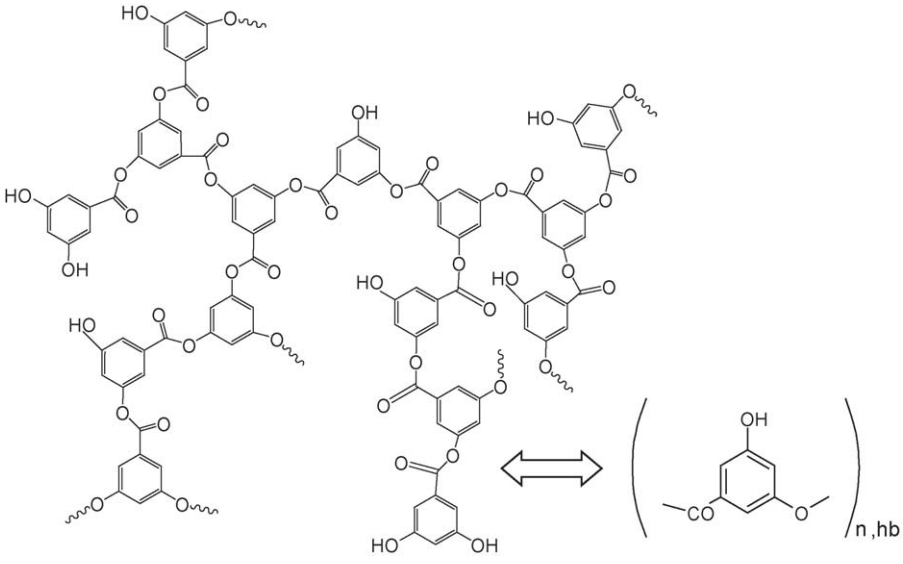

Fig. 1. Schematic representation of the hyperbranched aromatic polyester HBP-OH, based on the classic branched polycondensation approach [1].