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Relaxation induced optical anisotropy during dynamic overshoot swelling of zwitterionic polymer films

Wojciech Ogieglo [a], Joris de Grooth [a], Herbert Wormeester [b], Matthias Wessling [c], Kitty Nijmeijer [a], Nieck E. Benes [d,*]

[a] Membrane Science and Technology, Department of Science and Technology, Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
[b] Physics of Interfaces and Nanomaterials, Department of Science and Technology, Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
[c] RWTH Aachen University, Chemical Process Engineering Turmstrasse 46, 52064 Aachen, Germany
[d] Inorganic Membranes, Department of Science and Technology, Mesa+ Institute for Nanotechnology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

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ABSTRACT

In-situ spectroscopic ellipsometry was used to investigate the swelling behavior of thin supported zwitterionic polymers based on sulfobetaine methacrylate and n-butylacrylate. This material represents an interesting class of zwitterionic polymers, with large potential in reduction of biofouling of ultrafiltration membranes. It was found that the swelling rate and magnitude depend strongly on the content of zwitterionic groups incorporated in the polymer structure. Overshoot anomalous swelling dynamics were observed, explained by an interplay between enthalpic and entropic effects in various stages of the process. To elucidate the changes in the film properties a detailed ellipsometric analysis was conducted during polymer dilation and relaxation. For the polymer with 11.6 mol% zwitterionic groups, the thickness relaxation process after the swelling maximum is shown to be best described by a thin film with a time dependent uniaxial anisotropy. The behavior is rationalized via the orientations of polymer backbone and zwitterionic side chains, as a result of swelling and relaxation in the presence of the screening electrolyte.

1. Introduction

Polymers with incorporated zwitterionic moieties have gained a significant research attention due to their interesting potential application in a variety of fields, including oil recovery [1,2], ion chromatography [3], biocatalysis [4], removal of metal ions from water [5], drug delivery [6] and, recently, in membrane technology. When used for the modification of ultrafiltration membranes, zwitterionic moieties have been shown to greatly improve anti-fouling properties [7–14]. The resistance of membranes functionalized with zwitterionic groups towards biofouling is often explained by severe hindrance of cell adsorption on the modified membrane surface [15]. The same property is reported to be responsible for a very good blood compatibility of zwitterionic polymers, because of limited protein and blood platelets adhesion [16]. The implementation of zwitterionic groups into membrane polymers has been accomplished via routes of random copolymerization [7,8,10] or polymer modification [11–14] and already very low molar contents of zwitterionic groups (below 10 mol%) are reported to show a significant impact. In the case of zwitterionic polymers based on sulfobetaine methacrylate (SBMA) the explanations for the observed effects focus on the existence of self-assemblies of the zwitterionic moieties, which influence the character of hydrophobic-hydrophilic interactions within the polymer chains [17,18]. Such self-assemblies, based on dipole–dipole interactions between the zwitterionic side chains, have also been frequently reported to be formed in other similar polymers both in dry [19–21] and swollen states [22,23]. When the polymer is swollen in the presence of dissolved small molecule electrolytes these interactions are weakened. This is responsible for the so-called antipolyelectrolyte effect. It is manifested by an increase of chain expansion with increasing salt concentration as a result of screening of the dipole–dipole interactions by the small molecule electrolyte. Though the antipolyelectrolyte effect is relatively well understood on a qualitative level, there still seems to be a lack of understanding of the impact of specific small ions, polymer structure and other factors. In particular, little is known about the dynamics of the swelling behavior of zwitterionic thin polymer films in the presence of small molecule electrolyte.

A thin film geometry is especially beneficial in membrane applications, where the membrane separation performance is dictated by a dense polymeric layer (thickness ~ a few hundred nanometer), in contact with a fluid penetrant. In studies of thin and ultra-thin films, spectroscopic ellipsometry (SE) is a powerful technique. SE is based on the change of the polarization state of a specularly reflected light beam and has a very high sensitivity and accuracy for the determination of thin film properties such as thickness and refractive index. SE relies on changes in polarization state, rather than changes in light intensity. This makes it particularly suitable for measurements performed in-

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* Corresponding author. Tel.: +31 53 489 4288; fax: +31 53 489 4611.
E-mail address: n.e.benes@utwente.nl (N.E. Benes).

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situ, where the ambient might cause attenuation of light. There are a few studies in which in-situ SE has been applied to study swelling of polymer brushes [24], immobilized thin films [25] and polyelectrolytes [26] in liquid penetrant environment. The technique has also been used in dynamic water swelling of biocompatible zwitterionic polymers based on phosphorylcholine [27,28] and polyzwitterionic brushes on gold surfaces [29]. Similar studies are very rare and studies on dynamic swelling behavior of zwitterionic polymer thin films in the presence of strong small molecule electrolytes are not available.

In this work we use in-situ spectroscopic ellipsometry to study the dynamic swelling behavior of a thin film of supported zwitterionic random co-polymer of n-butylacrylate (nBA) and sulfobetaine methacrylate (SBMA) in the presence of an electrolyte (NaCl). The effect of the amount of zwitterionic monomer in the polymer is investigated and particular focus is put on the details of spectroscopic ellipsometry modeling of the swelling process. Various optical models, involving uniform, graded and anisotropic thin film representations are compared.

2. Spectroscopic ellipsometry

Spectroscopic ellipsometry measures the change in ellipticity of the reflected light, commonly quantified by the amplitude ratio Psi (Ψ) and the phase difference Delta (Δ), over a wide wavelength range. Deriving film properties from SE spectra requires the sample to be represented by an appropriate optical model that can be fitted to the experimental SE spectra. Generally the optical model involves a stack of multiple layers, each characterized by a thickness, h, and optical dispersion: the wavelength, λ, dependent refractive index, $n(\lambda)$, and extinction coefficient, $k(\lambda)$. For optically transparent dielectrics $k = 0$, and the optical dispersion is often accurately described by the Cauchy relation:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

where A, B and C are fit parameters.

The fit quality is evaluated based on the value of root Mean Square Error (*MSE*). For thin (100–200 nm) single layer uniform samples (dense SiO_2 on Si wafer) *MSE* values indicating a good fit are ~1–2. For thicker films, characterized by more complex morphologies, much higher *MSE* values (~10) are considered acceptable. Model modification (addition of fitting parameters, implementation of window corrections, etc.) is considered an improvement when the change in *MSE* is significant.

An appropriate optical model needs to be complex enough to capture the main characteristics of the sample, while overparameterization must be avoided [30]. The optical models used in this study are depicted in Fig. 1. The models comprise a crystalline silicon (100) wafer (with thin ~1.5 nm native oxide layer, not shown for clarity), supporting a polymer film that is in contact with an ambient: either a salt solution or air. The models differ in the description of the polymer film. In the uniform model (Fig. 1a) the film is considered to be isotropic and is characterized by a uniform refractive index, n_{pol} across its thickness. In the graded model (Fig. 1b), n_{pol} is allowed to be a linear function of the film thickness and the layer is divided into 5 equal thickness sublayers (the obtained value of n_{pol} corresponds to the middle sublayer). The last anisotropic model (Fig. 1c) considers the polymer film to be uniaxially anisotropic, with distinct n_z (perpendicular to the plane of the substrate) and $n_x = n_y$ (in the plane of the substrate).

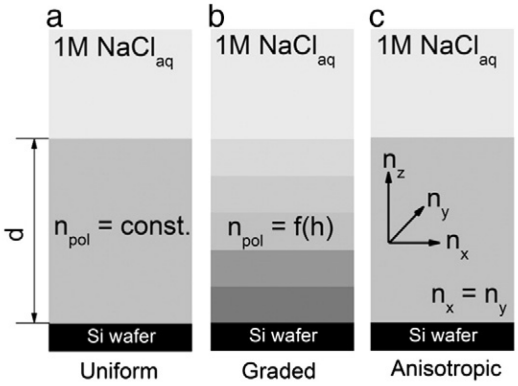

Fig. 1. Schematic representation of the optical models employed in this study.

In all of the optical models the refractive indices are fitted dynamically for the time resolved experiments. The values of refractive indices given in this work relate to the index at 632.8 nm.

3. Experimental details

3.1. Polymer synthesis and characterization

The nBA-SBMA random copolymer was prepared via a free-radical polymerization mechanism. A typical reaction involved the dissolution of 17.4 g nBA (135.7 mmol) and 5 g SBMA (17.9 mmol) in 100 ml of dimethyl sulfoxide in a 250 ml round bottom flask under a nitrogen atmosphere. The solution was heated to 70 °C, and subsequently 0.20 g $(NH_4)_2S_2O_8$ (0.9 mmol) was added. This mixture was left to react under reflux for at least 12 hours to ensure complete conversion of the monomers. After the reaction, the mixture was poured into demineralized water to form a precipitate. The precipitate was washed three times with 50 ml of water for 30 minutes and dried for 24 hours in a vacuum oven at 30 °C. The overall procedure gave the p(SBMA-nBA) copolymer (Fig. 2) with an 88% yield. The polymer was stored under vacuum and used without any other purification steps. The amount of added SBMA, relative to nBA, was tuned to obtain two polymer batches each with different content of the zwitterionic moieties.

Elemental analysis showed incorporation of 5.0 mol% and 11.6 mol% of the zwitterionic groups in the two polymer batches. Further in the text the two polymers are referred to as P1 and P2 respectively. The molecular weights of the obtained polymers were determined using size exclusion chromatography in tetrahydrofurane with 0.1 M LiCl against a polystyrene standard and resulted in M_w of approximately 55 kg/mol. Thermal stability of the copolymer was determined with thermogravimetric analysis (TGA 4000, Perkin Elmer) and no significant weight loss (<5%) was found until 300 °C. Differential scanning calorimetry (DSC 8000, Perkin Elmer) measured at 20 °C per minute showed one glass transition temperature at −37 °C. The results of the thermal characterization are comparable to those found in ref. [31].

3.2. Sample preparation and in-situ measurement procedure

Silicon wafers used as supports were cleaned by immersion in 98% H_2SO_4 with 30% H_2O_2 mixture (3:1 volume ratio) for 24 hours. Afterwards, they were flushed with demineralized water and ultra pure

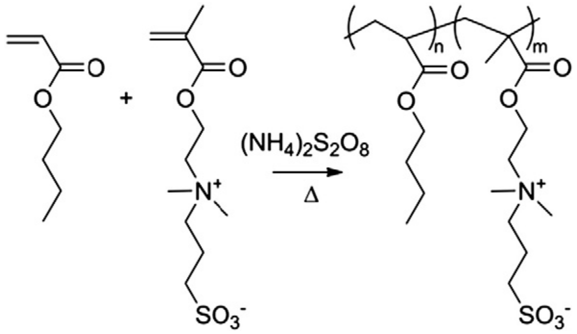

Fig. 2. Reaction scheme for the free radical polymerization of n-butyl acrylate (nBA) and sulfobetaine methacrylate (SBMA).