



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Xu, Wenyang; Mihhels, Karl; Kotov, Nikolay; Lepikko, Sakari; Ras, Robin H.A.; Johnson, C. Magnus; Pettersson, Torbjörn; Kontturi, Eero Solid-state polymer adsorption for surface modification: The role of molecular weight

Published in: Journal of Colloid and Interface Science

DOI: 10.1016/j.jcis.2021.07.062

Published: 01/01/2022

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version: Xu, W., Mihhels, K., Kotov, N., Lepikko, S., Ras, R. H. A., Johnson, C. M., Pettersson, T., & Kontturi, E. (2022). Solid-state polymer adsorption for surface modification: The role of molecular weight. *Journal of Colloid and Interface Science*, 605, 441-450. https://doi.org/10.1016/j.jcis.2021.07.062

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

Journal of Colloid and Interface Science 605 (2022) 441-450



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Solid-state polymer adsorption for surface modification: The role of molecular weight



Wenyang Xu^{a,b,*}, Karl Mihhels^a, Nikolay Kotov^c, Sakari Lepikko^d, Robin H.A. Ras^{a,d}, C. Magnus Johnson^c, Torbjörn Pettersson^{b,e,*}, Eero Kontturi^{a,*}

^a Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland

^b Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, 10044 Stockholm, Sweden

^c Department of Chemistry, KTH Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

^d Department of Applied Physics, School of Science, Aalto University, Espoo, Finland

e Wallenberg Wood Science Centre, Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 56, 10044 Stockholm, Sweden

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Article history: Received 26 May 2021 Revised 11 July 2021 Accepted 12 July 2021 Available online 21 July 2021

Keywords: Contact angle Dewetting Polymer adsorption Polystyrene Silicon wafers Surface modification

ABSTRACT

Hypothesis: Solid-state polymer adsorption offers a distinct approach for surface modification. These ultrathin, so-called Guiselin layers can easily be obtained by placing a polymer melt in contact with an interface, followed by a removal of the non-adsorbed layer with a good solvent. While the mechanism of formation has been well established for Guiselin layers, their stability, crucial from the perspective of materials applications, is not. The stability is a trade-off in the entropic penalty between cooperative detachment of the number of segments directly adsorbed on the substrate and consecutively pinned monomers.

Experiments: Experimental model systems of Guiselin layers of polystyrene (PS) on silicon wafers with native oxide layer on top were employed. The stability of the adsorbed layers was studied as a function of PS molecular weight and polydispersibility by various microscopic and spectroscopic tools as well as quasi-static contact angle measurements.

Findings: Adsorbed layers from low molecular weight PS were disrupted with typical spinodal decomposition patterns whereas high molecular weight (>500 kDa) PS resulted in stable, continuous layers. Moreover, we show that Guiselin layers offer an enticing way to modify a surface, as demonstrated by adsorbed PS that imparts a hydrophobic character to initially hydrophilic silicon wafers.

© 2021 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

E-mail addresses: wenyang.2.xu@aalto.fi (W. Xu), torbj@kth.se (T. Pettersson), eero.kontturi@aalto.fi (E. Kontturi).

https://doi.org/10.1016/j.jcis.2021.07.062 0021-9797/© 2021 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding authors at: Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland (W. Xu and E. Kontturi).

1. Introduction

Supported ultrathin polymer films are integral in versatile applications such as sensors, biomedical devices, organic solar cells, and organic thin film transistors [1–5]. Films with minute thickness can also be viewed as a means to modify the chemical and physical properties of a surface [6]. Film deposition can be performed by several methods, e.g., spin-coating, Langmuir-Blodgett deposition, chemical grafting approaches, [7–9] and combining self-assembled monolayers with binding a polymer layer [10–15].

Polymer adsorption is an attractive, yet little-investigated tool for actual film deposition or practical surface modification, as the vast literature on adsorption focuses largely on fundamental phenomena [16–22]. It is based on thermodynamic strive of polymer enrichment at interfaces, thereby omitting complex chemical reaction pathways, as shown in the pioneering works of McCarthy and coworkers who suggested to exploit adsorption as an actual means for surface modification for standard substrates like silica [23-28]. Recently, our group has established generic approaches for heterogeneous surface modification of lignocellulosic surfaces by polymer adsorption from aqueous and aprotic solvents [10,29,30]. The reason for the relatively esoteric status of utilizing adsorption as a modification medium lies perhaps in the outcome: polymer layers adsorbed from a solvent often exhibit incomplete coverage and their attachment on the substrate can be unsatisfactory in applications where long-term stability is required [29]. To tackle these deficiencies, we propose the utilization of lesser known solid-state polymer adsorption in the form of so-called Guiselin layers where the coverage is usually more comprehensive and the attachment firmer [31-33].

The formation of Guiselin layers has been well established since their existence was first proposed in 1992 [31]. A bulky polymer thin film larger than a few radii of gyration (R_g) is placed in contact with a substrate and annealed above the glass transition temperature (T_g) or melting point of the polymer, resulting in an irreversibly adsorbed ultrathin layer that remains on the substrate interface after the excess polymer has been rinsed out by successive leaching with a good solvent [16,17,22]. Guiselin layers have nearly exclusively been investigated within the realm of fundamental polymer physics, e.g., to unveil the adsorption mechanism or the formalism of the adsorption kinetics [17-19]. So far, the effect of the adsorbed layers on a number of materials properties has been investigated: glass transition, [22,34,35] diffusion coefficients, [36] thermal expansivity, [37] viscosity, [38] and crystallization ratio [39,40]. In this study, we want to transfer the concept of Guiselin layers into the territory of surface modification by exploring the film stability aside the standard properties, such as film thickness, coverage, and contact angle. Indeed, a crucial, yet not a fully addressed issue of Guiselin layers is their stability as ultrathin polymer films are susceptible to rupture during various treatments, e.g., elevated temperatures and solvent exposure which are inevitably present during the layer formation. This is particularly important given the issues with reproducibility of Guiselin layers, recently pointed out by Thees et al. [32] In addition, Gin et al. [17] have observed a density difference within the adsorbed polymer layer on a silicon substrate, prompting an inner area of higher density with a more flattened conformation named a 'lone flattened layer', [19] and an outer bulklike lower density area named a 'loosely adsorbed layer'. These flattened chains inhibit the penetration of free molecules causing autohydrophobic dewetting of thin polymer films at free polymer-adsorbed polymer interface, as shown in the comprehensive studies by Jiang et al.[41,42] Beena Unni et al., [43] in turn, showed that the adsorbed film stability significantly depends on the solvent used for washing out the excess polymer.

As a model system in this study, we use Guiselin layers of polystyrene (PS) on standard Si/SiO_x substrates. The idea is to show how Guiselin layers can be utilized as a means of stable surface hydrophobization of the silicon wafers. Concerning the polymer properties, we focused on molecular weight (M_w) and its effects on the formation and stability of PS Guiselin layers on silica substrates. The study differs from the existing stability studies on Guiselin layers [41–43] by its pragmatic approach as we pay particular attention to the relationship between film stability and the newly introduced hydrophobic properties.

2. Experimental parts

2.1. Materials

Toluene (>99.3%) and four PS grades were purchased from Sigma-Aldrich and used without further purification. The monodisperse PS grades are coded as PS30k (Mw ~ 32 000, Mn ~ 31 000) and PS560k (Mw ~ 524 000, Mn ~ 502 000). The polydisperse PS grades that are coded as PS35k (average Mw ~ 35 000) and PS192k(Mw ~ 32 000, PDI ~ 3.4) were analyzed by gel permeation chromatography (GPC), clearly showing bimodal distribution for PS35k (Table 1 and **Figure S1** in Supplementary Information). Silicon wafers with a native oxide layer 1.7 ± 0.2 nm, as measured by spectroscopic ellipsometry, were purchased from Okmetic Oy (Finland). Water used in this study was Milli-Q water (resistivity of 18.2 MΩ·cm, at 25 °C). All chemicals were used without further purification.

2.2. Preparation of substrate surface

The silicon wafers were cut to approximately 10 mm \times 10 mm prior to use. The wafers were cleansed by successive ultrasonic cleaning in Milli-Q water, acetone, isopropanol, and Milli-Q water. Subsequently, the wafers were dried under mild N₂ purge and further cleansed in UV/ozone chamber (Bioforce Nanosciences Inc., California, USA) for 15 min. The UV/ozone cleaning procedure has been shown to be an effective method to rapidly remove a variety of contaminants from surfaces and effectively decompose hydrocarbons.[44]

2.3. Deposition of polystyrene ultrathin films

The cleaned wafers were again purged with N₂ stream for dust removal and spin-coated with fresh toluene for final cleaning prior to film deposition. The atactic PS solutions were prepared in toluene (20 g/L). Thin films (thickness > few R_g , Table 2) were deposited by spin-coating (WS-650SX-6NPP/LITE, Laurell Technologies) the solutions at 4000 rpm for 90 s. The spin-coated films were annealed at 150 °C for 24 h under vacuum to promote adsorption and ensure equilibrium.[22,38] Subsequently, the films were transferred to a desiccator under air for cooling to ambient temperature. Further, the toluene leaching of the spin-coated polymer films was carried out in a systematic way by immersing the films every 10 min in 20 mL with fresh toluene at room temperature. The leaching procedure was successively carried out in onehour total, i.e., for 6 consecutive 10 min spans. Afterwards, the films were dried in vacuum oven at room temperature to remove solvent residue before analyses.

2.4. X-ray photoelectron spectroscopy (XPS)

XPS was performed in AXIS Ultra instrument (Kratos Analytical, UK). The samples were mounted on a linear sample holder with UHV compatible carbon tape and pre-evacuated overnight. A fresh

Table 1

Weight average molecule weight (M_w) and number average molecular weight (M_n) , polydispersity index (PDI) of PS35k and PS192k.

Sample	Peaks	M _w /Da	M _n /Da	PDI
PS35k	peak 1	1203	815	1.48
	peak 2	106 550	53 920	1.98
PS192k	peak 2	173 077	50 939	3.40

Table 2

Surface roughness and surface coverage after adsorption and thickness of the films after spin-coating and after adsorption by ellipsometry.

Sample code	Roughness* /nm	Surface coverage ^{&} /%	Thickness after spin-coating/nm	Thickness of adsorbed layer/nm
PS30k	0.78	63.4	60.0 ± 0.7	1.5 ± 0.1
PS35k	0.97	59.2	59.3 ± 0.6	1.8 ± 0.1
PS192k	0.93	79.6	73.0 ± 2.6	4.1 ± 0.9
PS560k	0.29	100.0	111.8 ± 0.7	5.4 ± 0.2

* The Root mean square roughness, Rq values, are extracted from AFM with area of 5 μ m imes 5 μ m.

[&] Surface coverage is derived from AFM image using ImageJ software package.

piece of pure cellulosic filter paper (Whatman 1) was mounted and analyzed with each sample batch as an *in situ* reference.[45] Measurements were performed using monochromated Al K α irradiation at 100 W and under neutralization. Wide energy-range scans using 80 eV CAE AND 1 eV step, as well as high resolution scans of C 1 s, using 20 eV CAE and 0.1 eV step were recorded on 3–4 locations for each sample, with nominal analysis area of $400 \times 800 \ \mu\text{m}^2$. Data analysis was performed using CasaXPS software. Charge corrected wide scans were used for elemental analysis. Conditions in UHV remained satisfactory throughout the analysis. The low and stable contamination levels observed in the *in situ* reference sample, which was measured before and after each experiment, justified the analytical use of the C–C component in high resolution C 1 s spectra.[46]

2.5. Ellipsometry

Ellipsometry was performed on a J. A. Woollam M2000UI (Lincoln, United States) spectroscopic ellipsometer with auto retarder and rotating analyzer setup at incident angles of 60° and 70° . The measurements were performed in the spectral range from 245 to 1690 nm wavelength. The data evaluation was carried out using CompleteEASE (ver. 6.51) software. For the fitting of the real part of the refractive index $n(\lambda)$ in all determined layers, a Cauchy model was assumed:[47]

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

where λ is the wavelength of radiation in micrometers. A, B and C are the Cauchy coefficients and they are all fitted as positive values. The imaginary part for the complex refractive index was assumed negligible. For the complex refractive index of the silicon substrate and the silicon oxide layer, software data have been used as listed in the software database. To reduce the number of free parameters, the thickness of the oxide layer was determined before the deposition of the organic layer. The thickness evaluations of the deposited film after spin-coating and adsorbed layer after solvent leaching were performed with a fixed value of oxide layer for each sample. All measurements were carried out under mapping mode, measuring 9 discrete points for each sample. At least triplicates were done for each batch of samples. The reported average values and relative standard deviations are computed upon the abovementioned 9 points.

2.6. Atomic force microscopy (AFM)

The surface topography of the spin-coated and residual films was collected through a Multimode 8 AFM from Bruker AXS Inc. (Madison, WI, USA) in air. Images were taken with a J scanner in tapping mode using NSC15/AIBS silicon cantilevers from Mikro-Masch (radius of 8 nm, resonance frequency 325 kHz, Tallinn, Estonia). A minimum of three images were taken per sample, and scans were performed over several portions of the films. Other than a simple first order flattening, no image processing was carried out. For image analysis, the extracted images were subjected to ImageJ thresholding by Otsu's method[48] producing binary images, in which the adsorbed layers (crests) and void spaces (troughs) correspond to white and black areas, respectively.

2.7. Nanoscale infrared imaging and spectroscopy

The experiments were performed using a scattering-type scanning near-field optical microscope (s-SNOM) from Neaspec GmbH (Germany). In the setup, the atomic force microscope (AFM) works in tapping mode providing topography images of the sample surfaces. The AFM tips (Arrow NC-Pt from Nanoworld, Germany) were made of a silicon core that was coated with a Pt:Ir alloy (radius ~ 20 nm, resonance frequency 285 kHz). The tapping amplitude was maintained at 30 nm when the tip was in contact with the sample surface. The metal alloy coating of the AFM tip makes it suitable for nano-FTIR spectroscopy and infrared pseudoheterodyne imaging. A description of these methods can be found in these references.[49-51] Importantly, the pseudo-heterodyne detection technique allows a background-free accumulation of near-field optical images and provides images of both the "amplitude" relating to the reflectivity and the "phase" relating to the infrared absorption. These optical images are acquired simultaneously while obtaining the AFM topography image.

With s-SNOM the complex scattering coefficient can be obtained by a Fourier transform of the interferogram of the signal for each harmonic *n* of the vibration of the AFM tip, and the second harmonic was used in this study. To obtain s-SNOM images a scanning speed of 12.3 ms per pixel was employed and the AFM tip was illuminated by a quantum cascade laser (QCL) at 1500 cm⁻¹ set to 0.3 mW output power.

The nano-FTIR spectra were acquired with a tuneable femtosecond broadband laser (at repetition frequency 80 MHz, output power 0.14 mW, spectral range 950–1950 cm⁻¹), generating the broadband IR light by employing DFG crystals. The nano-FTIR spectra have a spectral resolution of 12 cm⁻¹, the number of scans was 10 with 9.8 ms integration time per scan. To compensate for the wavenumber-dependent laser energy, water vapor, carbon dioxide, absorption in optical components in the system etc., the nano-FTIR spectra were normalized to a background spectrum acquired at a silicon wafer using a reference calibration grating TGQ1 sample. All AFM and s-SNOM images (including all modes) were levelled and plane-fitted using the Gwyddion software (v. 2.55 for Windows - Czech Metrology Institute, Czech Republic).[52]

2.8. Contact angle goniometry

Contact angles of the modified surfaces with water (static, advancing and receding) were measured using a Theta Flex optical tensiometer (Biolin Scientific, Sweden). Static water contact angle was recorded at 10 s after placing a sensile water drop on the sample surface. Quasi-static contact angles, i.e., advancing and receding contact angle, were measured using needle-in-the-sessile-drop method.[53] Contact angles were measured with two points per substrate. At least triplicates were done for each batch of samples. The reported average values and relative standard deviations were determined based on the abovementioned six points.

3. Results and discussion

3.1. Surface chemistry and morphology

Fig. 1a represents the XPS wide-range spectra with conspicuous carbon emission indicating the irreversibly adsorbed PS layer on Si/ SiO_x substrate after annealing at 150 °C and subsequent solvent leaching. High-resolution XPS data in Fig. 1b depicts the adsorbed PS on the silica surface. It is noteworthy, that the band integration for 560 K was clearly higher than for other samples. In our analysis, all the spectra were referenced to the most intense PS peak present at 284.8 eV where the prominent contribution of saturated C 1s emission is typically identifiable in hydrocarbons.[16,54,55] The shake-up peak, corresponding to the π - π ^{*} transition of the aromatic ring in PS with a binding energy between 291.0 and 293.0 eV, is also clearly discernible especially for the layer of PS560k. The quantitative analysis performed on the spectra of the C 1s band is suggesting increased adsorption onto silicon surface with different PS molecular weights. However, the PS192k intensity is slightly lower than PS35k, which is likely associated with the specific surface coverage in the XPS measuring area. Nevertheless, silicon emission (Si 2p at 100 eV) is distinctive for all samples after adsorption in the wide-scan spectra, which indicates that the adsorbed Guiselin layers are not thicker than few nanometers because the escape depth of photoelectrons in XPS is at most 3-10 nm. The minute thickness was more precisely demonstrated by ellipsometry (see, Table 2). It is noteworthy that after spincoated and annealed PS on silica – that is, before annealing to form the Guiselin layers and subsequent rinsing - the silicon emission is not observed in the XPS spectra (Figure S2). The reason for the lack of the silicon contribution is that the spin-coated PS layers are thicker than the probing depth of the XPS, i.e., >10 nm (see, Table 2).

It is also notable that the background of Si 2p and Si 2 s emission in the region between 100 and 200 eV changes with different M_w of PS after adsorption (Fig. 1a inset). According to the formalism of peak shape on surface morphology, as described by Tougaard et al.,[56] the shape of the band background is reflecting the extent of PS coverage on silica surface. In Fig. 1a, the adsorbed PS layer with PS30k and PS35k represented similar results with raised silicon band background, suggesting a partial surface coverage by the adsorbed PS. Meanwhile, the silicon contribution in



Fig. 1. X-ray photoelectron spectroscopic wide scan of adsorbed PS thin films with different M_w after solvent leaching after annealing at 150 °C for 24 h, as well as the insets presenting the silicon peak background, and O KLL and O 2s peaks (a), and high-resolution C 1s scan of the adsorbed PS thin films (b).

PS560k is also visible, but the signal is dampened by the layer of PS covering the silicon surface. Moreover, the loss of the O KLL Auger signal at around 1000 eV suggests a fully covered substrate, as the oxygen Auger electron escape depth is between 1 and 2 nm. [57] The emitted electrons are prevented from escaping by a continuous layer of PS560k compared to the PS30k and PS35k samples where the Auger signal does appear. In the same vein, the presence of Auger signal of the adsorbed PS192k is indicative of a partial coverage as the Auger electrons can still escape.

AFM topographies of the samples having the adsorbed PS after annealing and subsequent solvent rinsing with varying M_w are consistently supporting the XPS observations of either partial or full coverage. Morphologically, a typical spinodal dewetting scenario,[58–60] i.e., the breakup of a thin film occurring through the growth of uniformly distributed surface undulations, was observed when M_w values below 192 kDa were used in the process (Fig. 2 (a-c)). Generally, the film stability increases as the polymer M_w increases, that is, the observation of crests and troughs is less dominant. In contrast to low M_w PS, the adsorbed layer of PS560k (Fig. 2(d)) is a smooth film with topographic roughness at around 3 Å (Table 2). Our findings of low M_w PS are at odds with several other reports on homogeneous layers after solid-state



Fig. 2. The topography images of representative Guiselin layer films of PS30k (a), PS35k (b), PS192k (c), and PS560k (d) with integrated height profiles. It is noteworthy that the spinodal decomposition occurred with not always repeating the exact same dewetting topography for the films of PS30K, PS35k, and PS192k.

adsorption where a full coverage with a certain thickness, as measured by ellipsometry, is at least implicitly described [16,17,61,62].

As reported previously, the formation of Guiselin layers is governed by a monomer pinning mechanism (molecular motion), interfacial potential, available adsorption sites, and annealing time [32,33,61]. As the extent of adsorption increases, the space available for monomer pinning reduces. The chains adsorbed at low surface coverage create a potential opposing the growth of the interfacial layer. New chains need to stretch before diffusing through the layer formed by the molecules at surface. In this regard, the correlated reduction in the number of allowed configurations yields a severe entropy loss [63]. From the point of view of free energy, the formation of the adsorbed layers is determined by the competition between a gain in adsorption energy (monomer pinning) and the loss of conformational entropy of the chain [61,63]. Collectively, a homogeneous and flat polymer thin layer with a designated thickness after adsorption can be manipulated within the Guiselin layer construction, as confirmed by PS560k (Fig. 2 (d)). However, the conformational entropy of low molecular weight polymer in melt is greater than high-molecular-weight polymer, resulting in higher instability of the adsorbed film of PS30k, PS35k, and PS192k (Fig. 2 (a-c)). Higher instability is also evident from the ellipsometry data, showing apparently thinner layers for lower M_w PS grades (see, Table 2), in line with the AFM images of Fig. 2.

A bicontinuous, partially dewetted surface of the adsorbed layers on Si/SiO_x substrate was also observed by Napolitano et al. [18,64] In their studies, a short annealing time (no exact annealing time mentioned) was associated to the rupture surface. However, an annealing time of 24 h in our study followed the criterion on equilibrium, as postulated for polymer chain conformations on a solid substrate using polymers of diverse M_w (123-2000 kDa) [17,22]. Periodically distributed crests and troughs were found in the adsorbed layer of monodisperse PS30k (Fig. 2(a)) after annealing and toluene solvent leaching. This is supported by Jiang et al. [41] observing the occurrence of spinodal dewetting of the adsorbed layer when the used polymer M_w is below critical $M_{\rm w}$ = 123 kDa. Jiang et al. postulated that the loosely adsorbed chains with short chains (M_w < 50 kDa) could be easily removed during solvent leaching due to their low desorption energy upon the small number of segment-surface contacts. It is also apparent that the single crest area was bigger with polydisperse PS35k (Fig. 2(b)). This could be induced by the adsorption of long molecules (larger M_w) as a 'connector' suppressed dewetting in the case of PS35k, as reported by Raphaël and de Gennes, [65] Reiter et al., [66,67] as well as Koga and coworkers [41,42]. However, the bimodal M_w distribution of PS35k with both M_w are below 123 kDa, which could not aid to form a full surface coverage after solvent rinsing.

Hence, it is surprising to observe a dimple structure when a polydisperse PS with M_w of 192 kDa is used, though the spinodal dewetting behavior was also observed when a monodisperse PS with M_w of 136 kDa (higher than 123 kDa in Jiang's study) was used by Beena Unni et al. [43] Nevertheless, it is apparent that the continuous phase of the adsorbed layer increased which is revealed by an increased total surface coverage to around 80%. We may conjecture that M_w and polydispersity both play a significant role in surface dewetting after polymer adsorption. Given the trough depth of around 5 nm in Fig. 2(c), we scrutinized the possible existence of highly dense adsorption layer in the trough area in the following section.

3.2. Nanoscale infrared imaging and spectroscopy

Nano-FTIR, a recently developed technique, with a nanoscalelevel spatial resolution by combining IR spectroscopy and s-SNOM was employed to study the surface coverage at 20 nm length scale [68]. To obtain a reference for a nano-FTIR spectrum of PS, the adsorbed layer of PS560k was studied since it formed a



Fig. 3. Nano-FTIR spectra acquired at random places on the sample PS560k. All spectra show the characteristic bands at around 1450 and 1500 cm⁻¹.

continuous and a relatively thick layer on the substrate in comparison to the other samples. The obtained nano-FTIR spectra (Fig. 3) displayed two characteristic IR absorbance bands of PS at around 1450 and 1500 cm⁻¹, demonstrating a good agreement between the band positions in nano-FTIR and conventional IR spectroscopies [69–71]. Despite the extremely low thickness of the PS film (ca. 5 nm), clear bands were observed, hence highlighting the capability of the instrument to provide spectra of ultrathin films with a spatial resolution on the nanoscale. Nevertheless, due to the relative minute thickness of the PS film, the signal-to-noise ratio in the acquired nano-FTIR spectra is sufficiently low to unambiguously observe other PS bands in this spectral region.

Since s-SNOM imaging offers an excellent optical spatial resolution of around 20 nm, it was possible to study the distribution of PS192k over the Si wafer. Based on the PS absorption peak in nano-FTIR spectrum of the PS560k sample above (Fig. 3), the band at around 1450 cm⁻¹ in the spectrum is more intense in contrast to the band at 1500 cm⁻¹, whereas the laser energy at 1450 cm⁻¹ is significantly lower. Therefore, s-SNOM imaging was performed at 1500 cm⁻¹ wavenumbers to investigate the possible optical (and thus chemical) contrast representing surface coverage.

The acquired s-SNOM optical images reveal a clear heterogeneity in the amplitude (Fig. 4(c)) as well as in the phase image (Fig. 4 (d)) between the Si wafer and polystyrene. The Si wafer is a highly reflective surface and hence the polystyrene domains in PS192k (represented by higher areas in the AFM topography image) exhibit a lower reflectivity in the amplitude image, as revealed by lower amplitude values. In contrast, these polystyrene domains have a higher phase, which is indicative of an enhanced IR absorption at 1500 cm⁻¹. The acquired images in Fig. 4 (AFM and s-SNOM) correspond very well to each other, thus confirming that polystyrene in PS192k is concentrated in domains of ca. 3-5 nm height (based on AFM data) separated with areas depleted of polystyrene. However, because the s-SNOM images show only relative changes, there is a possibility that trace amounts of polystyrene remain on the bottom of the troughs. In principle, nano-FTIR spectra could reveal the presence of polystyrene in the troughs, but for the PS192k film that is thinner than the PS560k film in Fig. 3, no signal above the noise level was observed neither at the domains nor in the troughs. In general, the chemical contrast seen in the obtained



Fig. 4. A representative AFM topography map of PS192k a) $5 \times 5 \ \mu m$, b) $1 \times 1 \ \mu m$ and c) s-SNOM 2nd harmonic optical amplitude image (a.u.); d) s-SNOM 2nd harmonic optical phase image (rad.). The s-SNOM images were acquired using the QCL laser tuned to emission at 1500 cm⁻¹ wavenumbers.

s-SNOM images agrees with the above XPS data and indicate that low M_w polystyrene, contrary to PS560k, has tendency to disrupt the continuous layer, following the spin-coating on Si wafers and the subsequent heat and solvent treatments, as discussed previously.

3.3. Layer thickness

The thickness of the layers before and after adsorption was measured with spectroscopic ellipsometry considering a simple multilayer model, air/PS/SiO₂/Si (substrate). More detailed parameters and fittings regarding the model are revealed in Figure S3. The accuracy of the thickness evaluation by ellipsometry was complemented by AFM scratching approach in the case of smooth, continuous films from PS560k. According to AFM, the thickness of the adsorbed PS560k was ca. 5 nm (Figure S4), which is comparable to the value from ellipsometry, i.e., 5.4 nm. However, the high roughness value (Table 2) of the rupture surface with lower $M_{\rm w}$ might cause less accuracy of the fitted thickness data [18]. With regard to the rupture surfaces, the thickness is closer to the average thickness rather than the maximum thickness due to the existence of troughs or voids on the surface. Moreover, the sensitivity of ellipsometry is generally considered to decrease in films below 10 nm. Nevertheless, ellipsometry was able to distinguish thickness values ranging from 1 nm to 5 nm (Table 2).

3.4. Film stability

The film stability is increasingly important when considering the possible applications of the adsorbed layer. Heterogeneous dewetting may cause film instability at all stages of Guiselin layer formation, i.e., spin-coating, annealing, [34] and solvent leaching [43,72]. It is triggered by the presence of omnipresent heterogeneities, e.g., dust particles or defects at the substrate surface [73]. Thus, in this study, the silicon wafers were carefully cleansed to remove hydrocarbon contaminants and dust particles on the surface to minimize the possibility of heterogeneous dewetting. Without major heterogeneities, the films may dewet in a spinodal scenario, [58-60] i.e., by the amplification of capillary wave fluctuations of specific wavelength, often enhanced by the native oxide (SiO_x) layer at the substrate-polymer interface. As mentioned earlier, annealing time with temperature above the T_g was agreed as one of the crucial factors to facilitate the film stability on the substrate. Apart from that, solvent washing including washing time and solvent choice is debated as another factor provoking the morphology of the adsorbed layer. For example, Beena Unni et al. [43] found that the adsorbed layers underwent spinodal dewetting at different time scales of rinsing upon solvent polarity. The use of different solvents results in varied transition layer thickness below which the flat film turns to spinodal dewetting. When toluene was used as a good solvent for PS, the experimental transition thickness was determined as ca. 2.8 nm. Conversely, Davis et al. [72] have recently demonstrated that the thickness of the adsorbed PS layer is insensitive to the used solvent type.

All in all, the film stability can be originated and mathematically described by the Lifshitz-van der Waals interaction potential. The interfacial potential is reconstructed from references [59,73] in Fig. 5 for SiO_x/PS/air system with a 1.7 nm SiO_x layer, i.e., similar to the thickness of a native oxide layer in silicon wafers used in this study. As established in the system of SiO_x/PS/air, the interfacial potential can be written: [59,74]

$$\Phi(h) = \left(\frac{-A_{SI/PS/Air}}{12\pi(h+d_{SIO_X})^2}\right) + \left(\frac{-A_{SIO_X/PS/Air}}{12\pi h^2}\right) - \left(\frac{-A_{SIO_X/PS/Air}}{12\pi(h+d_{SIO_X})^2}\right)$$
(2)

where, h is the film thickness; d_{SiOx} is the thickness of silicon oxide layer, and $A_{Si/PS/Air}$ and $A_{SiOx/PS/Air}$ stand for the effective



Fig. 5. Effective interfacial potential Φ (h) and the curvature of the interfacial potential (Φ " (h)) for PS films on a silicon wafer with a native, 1.7 nm SiO_x layer between PS and silicon, reconstructed according to references[59,73].

Hamaker constants of the Si/PS/Air and the SiO_x/PS/Air systems, respectively. According to literature, the $A_{SiOx/PS/Air}\xspace$ is not well defined, ranging from -0.22 to 1.6×10^{-20} J [62]. In this case, the curvature (second derivative) of the interfacial potential is normally considered, defining that at Φ " (h) > 0 are metastable films and do not dewet whereas at Φ " (h) < 0 are unstable [75]. In this study, the thickness of SiO_x layer at ca. 1.7 nm does not cause dewetting when the PS film thickness is over 3 nm (film thickness after spin-coating in Table 2) due to the sign of Φ " (h) which is positive for a metastable film (Fig. 5) [62]. As another non-negligible postulation, the residual stress generated after spin-coating is also a possible driving force for dewetting. Reiter et al. [76] found that residual stresses are estimated to be on the same order of magnitude as the acting capillary forces on the course of annealing above T_{g} . However, the heterogeneities, the presence of the native silica layer, and the residual stress from spin-coating would only cause dewetting throughout the entire spin-coated film, instead of merely occurring in the underlying layer in the vicinity of the silica surface (i.e., in the Guiselin layer). Here, the spin-coated films after annealing were intact according to AFM topography (Figure S5).

In contrast to the whole spin-coated film, the thinner Guiselin layer may be more labile, particularly upon its formation under elevated temperature. The adsorbed layer may play a distinct role of a mobile phase apart from the bulk material causing density variation [17,19] and surface undulations during annealing [21,37]. As a result, a property difference abounds between the adsorbing/adsorbed layer and the outer bulklike part. In other words, we must consider a system SiOx/PS (Guiselin)/PS (bulk)/ air instead of the conventional SiOx/PS/air (eq. 2) during solid state adsorption. Recently, Li et al. [77,78] showed that the chain evolution of the irreversibly adsorbed layer during annealing process caused entropic inequivalence, resulting in macroscopic dewetting of the entire thin film (thickness of 250 nm) upon prolonged annealing of 120 h. The relatively short annealing time of 24 h in this study may merely promote the dewetting of the adsorbed Guiselin layer, not the dewetting of the whole spin-coated film. According to literature, [16,18] the PS30k and PS35k will show thickness equilibrium (i.e., namely the asymptotic plateau value of the residue thickness upon long annealing times) of 2.6-2.8 nm, which is comparable to the ellipsometry study in our case. Supported by the interfacial energy, the adsorbed PS30k and PS35k with thickness below 3 nm (Table 2) presented a dewetting pattern at the presence of SiO_x layer at ca. 1.7 nm, as revealed in Fig. 2(a) and 2(b), respectively. Simultaneously, it was postulated that the adsorbed Guiselin layer could partially 'migrate' to bulk phase during film cooling stage after annealing due to its greater entropy

gain for lower molecular weight polymers [79]. As judged by the adsorbed layer thickness on the interfacial energy theory, the adsorbed PS192k (Fig. 2(c)) should be as stable as PS560k (Fig. 2 (d)). However, the low molecular fraction and polydispersity of PS192k (Figure S1) may interfere with the adsorption behavior. More systematic study on the film stability of using polydisperse polymers should be considered. Furthermore, the stability of PS560k Guiselin layer after the deposition was verified to check the effect of annealing on the stability of the adsorbed layers. The PS560k Guiselin layer was post-annealed for another 24 h and found unstable with heterogeneous dewetting (Figure S6) instead of wavelength-dependent spinodal dewetting. As the heterogeneous dewetting resulted in a relatively low abundance of troughs, however, its effect on the contact angle with water (Table 3) – i.e., on the actual extent of surface modification – was minimal. All this suggests that the adsorbed Guiselin layer is a stable and 'not dead' adsorbed laver on the substrate, which is consistent with the dewetting or instability of the formed Guiselin layer after post-annealing [62]. Therefore, the adsorbed Guiselin layer is a 'living layer' under the annealing process, which may easily promote the occurrence of dewetting in the adsorbed polymer layer especially with low molecular weight and polydispersity.

3.5. Water contact angles

The hydrophobizing effect of the adsorbed polymer layer is prominent as the water contact angles of the treated silicon wafers show in Table 3 and Figure S7. The static contact angles of the adsorbed polymers with different PS $M_{\rm w}$ values are around 90°. This is a prominent comparison with the cleansed hydrophilic silicon wafer which, when untreated, is effectively wetted by water (Figure S7a) and showing near-zero contact angles (below 5°) – a fact well established [80,81]. It should be mentioned that the water contact angle of the pristine, bulky PS directly after spincoating (ca. 100 nm) is around 92° in this study (Figure S7b, Table 3), serving as a comparative reference for the adsorbed thin layers. It is clear that the Guiselin layers of PS192k and PS560k present a value close to that of a thick pristine PS film (ca. 100 nm), indicating a successful alteration of surface hydrophobicity, indeed a reversal from hydrophilic to hydrophobic. The slight variation of the measured static contact angle of PS film in air can be associated as polymer thickness-dependent effect, governed by the longrange van der Waals forces from the underlying substrate and the topography roughness [82]. This unambiguously illustrates the efficiency of Guiselin layers, particularly with high $M_{\rm w}$ PS560k, to completely alter the surface properties of silicon wafers from highly hydrophilic to hydrophobic. One could think of utilizing Guiselin layers as an alternative to self-assembled monolayers

Table 3

Static, advancing θ_a and receding θ_r contact angles of water on the adsorbed PS with different molecular weights.

Thin films on silica	Static contact angle*, θ _s /°	Advancing / receding contact angles, θ_a/θ_r (°/°)	Contact angle hysteresis, $\theta_a - \theta_r/^\circ$
PS30k	89.0 ± 1.8	94.3 ± 0.1/72.5 ± 0.3	21.8
PS35k	90.9 ± 0.3	95.2 ± 0.2/76.2 ± 0.5	19.0
PS192k	91.2 ± 0.4	97.2 ± 0.4/82.1 ± 0.4	15.5
PS560k	91.0 ± 0.4	96.9 ± 0.3/82.1 ± 0.2	14.8
PS560k_spin- coating	92.1 ± 0.2	96.2 ± 0.2/82.1 ± 0.1	14.1
PS560k Guiselin layer_post-	92.1 ± 0.2	95.8 ± 0.3/81.4 ± 0.2	14.4

* The contact angle is measured 10 s after the sessile drop was placed on the sample surface.

Table 4

Com	parison among	different	surface	modification	approach	for solid	substrate	in the	viewpoint	of their	processes a	and main	features.

Process [reference]	Description	Requirements on the substrate	Requires custom-built instrument
Plasma treatment [84]	Bombarding substrate with electrons and ions under plasma	-	Yes
Coating technologies	Wide variety of methods to form a film by precipitation on a solid surface; usually results in thick and rough films	-	Not necessarily
Spin coating [85]	Sub-category of coating for controlled deposition of smooth, ultrathin films	Must be non-porous	Yes
Chemical vapor deposition (CVD) [86]	Wide variety of deposition techniques of gaseous substances on solid surfaces	Must be reactive with the coating species	Yes (for controlled deposition)
Self-assembled monolayers [83]	Chemisorption of surfactant head groups, followed by a tail organization	Must be reactive with the head groups	No
Langmuir-Blodgett technology [87]	Monolayer by monolayer deposition of (usually) organic material from liquid-gas interface to solid substrate	Planar substrate required	Yes
Layer-by-layer deposition [88]	Films formation by depositing alternating layers of oppositely charged polyelectrolytes or colloidal particles	Requires attractive interactions (often opposite charge) with coating polymers	Not necessary (labor- intensive without one)
Guiselin layer deposition [this study]	Thick film deposition followed by annealing above glass transition temperature and fresh solvent leaching	No	No

(SAMs) which generally require a reactive interface to form [83]. A comparison among different modification approach for a solid surface is listed in Table 4. Since the formation of Guiselin layers is driven by thermodynamic strive, [18] the chemical match between the substrate and the coating is irrelevant, i.e., no demanding requirement of reactive substrate. As a result, virtually any substrate/polymer combination is feasible as long as the substrate can withstand the annealing and solvent leaching.

The advancing and receding contact angles were measured for the evaluation of the surface roughness and chemical heterogeneity, as revealed by hysteresis. Table 3 shows how the water contact angle hysteresis decreases as the surface coverage of PS increases with high M_{w} . As a general trend, the water contact angle hysteresis showed a decreasing tendency with higher surface coverage upon the increase of the applied PS M_w . This is a result of the surface rupture of low M_w polymers as observed by both AFM (Fig. 2) and XPS (Fig. 1), and altogether the hysteresis is more sensitive to the distinction among Guiselin layers of different $M_{\rm w}$ than the mere contact angles. However, as indicated by the calculated water contact angles (Table S1) with the hypothesis of Cassie-Baxter state [89] using the analyzed surface coverage, the current surface dewetting pattern should fit the Wenzel state. Therefore, we may doubt the accuracy of the obtained surface coverage of AFM images in particular with PS192k (Table S1). We may still conjecture that PS segments are probably underlying the troughs and cover the rupture area as shown in AFM images, despite intensive surface coverage studies of PS192k via surface sensitive techniques, i.e., XPS and Nano-FTIR pointing otherwise.

4. Conclusion

In this study, the solid-state adsorption was revisited according to the well-established Guiselin process [31] with the emphasis on application for surface modification. The existence of the adsorbed layers was established by monitoring the surface chemical composition with XPS. Contrary to several other accounts, [16,61,62] however, the adsorbed layers presented typical surface spinodal dewetting with molecular weight dependence, as revealed by AFM. The thickness of the adsorbed layers was investigated on average by ellipsometry in the range of 1.5 to 5.5 nm without considering the surface roughness. On the basis of previous investigation on the film stability upon the effect of M_w in the systems of monodispersed polymers determined by interfacial potential difference and density variations within the adsorbed layer, [21,41,42,62] the spinodal dewetting during Guiselin layer forma-

tion did not appear to relate to polydispersity when M_w was lower than 192 kDa in this study. However, an exhaustive study with wide-spectrum M_w of bimodal polymers concerning film stability would be interesting to perform in the future. The surface coverage of polydisperse PS192k was exceptionally found to be incomplete as agreed by surface sensitive imaging and spectroscopic techniques, i.e., AFM, XPS, and Nano-FTIR. Yet the inscrutably similar water contact angle of PS192k layer with a ruptured surface compared to that of PS560k layer with homogeneous coverage raised questions for future studies where, e.g., density profile analysis by neutron reflectivity could provide answers on whether minute amounts of polymer exists in the troughs of the ruptured layers [90]. Nevertheless, the prominent hydrophobizing effect of the adsorbed PS indicated that ultrathin Guiselin layers are premium candidates for surface modification. The results here indicate that Guiselin layer deposition is a viable route to modify planar surfaces and it can readily compete with, e.g., deploying specific solutionbased chemical reactions or utilizing chemical vapor deposition, as shown here by changing the properties of initially hydrophilic Si/SiO_x into a clearly hydrophobic surface. Generically, a smooth surface coating or a confined surface pattern can be manipulated through solid-state adsorption with employing an appropriate polymer molecular weight with consideration of polydispersity. However, adsorption stability with consideration of Lifshitz-van der Waals interaction potential should be considered while performing surface adsorption on different substrate/polymer systems. All in all, Guiselin layers represent a new, competitive approach for surface modification of diverse solid substrates with a wide spectrum of possible polymers. It stands the test with other conceptual methods for surface modification, as elaborated in Table 4. Therefore, we foresee that the full potential of polymer adsorption and Guiselin layers, in particular as a means for surface modification and functionalization, is yet to be established.

CRediT authorship contribution statement

Wenyang Xu: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Writing – original draft. Karl Mihhels: Investigation, Validation. Nikolay Kotov: Investigation, Formal analysis, Validation. Sakari Lepikko: Investigation, Validation. Robin H.A. Ras: Methodology, Validation, Writing – review & editing, Supervision, Resources. C. Magnus Johnson: Investigation, Formal analysis, Resources, Validation. Torbjörn Pettersson: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Eero Kontturi:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

W.X. acknowledges the funding from Tandem Forest Values (Project STRONGAD). Prof. Pekka Peljo is thanked for helping with contact angle measurements. Olle Engkvists Stiftelse (Sweden) is acknowledged for funding the nano infrared microscope as well as a postdoc scholarship for K.N. Dr. Leena-Sisko Johansson is thanked for assisting with XPS analyses and data interpretation. Dr. Katja Heise is thanked for helping with GPC measurements. Dr. Zhuojun Meng and Tao Zou (M.Sc.) are thanked for valuable discussions. This work made use of Aalto University Bioeconomy and RawMatters Facilities. We also acknowledge the provision of facilities and technical support by Aalto University at OtaNano - Nanomicroscopy Center (Aalto-NMC). The study is a part of Finn-CERES Materials Bioeconomy Ecosystem.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.07.062.

References

- B. Adhikari, S. Majumdar, Polymers in sensor applications, Prog. Polym. Sci. 29 (7) (2004) 699–766.
- [2] A.L. Hook, C.-Y. Chang, J. Yang, J. Luckett, A. Cockayne, S. Atkinson, Y. Mei, R. Bayston, D.J. Irvine, R. Langer, D.G. Anderson, P. Williams, M.C. Davies, M.R. Alexander, Combinatorial discovery of polymers resistant to bacterial attachment, Nat. Biotechnol. 30 (9) (2012) 868–875.
- [3] S. Günes, H. Neugebauer, N.S. Sariciftci, Conjugated polymer-based organic solar cells, Chem. Rev. 107 (4) (2007) 1324–1338.
- [4] G. Li, R. Zhu, Y. Yang, Polymer solar cells, Nat. Photonics 6 (3) (2012) 153–161.
- [5] C. Kim, A. Facchetti, T.J. Marks, Polymer gate dielectric surface viscoelasticity modulates pentacene transistor performance, Science 318 (5847) (2007) 76– 80.
- [6] G. Reiter, J. Forrest, Special issue on properties of thin polymer films, The European Physical Journal E 8(2) (2002) 101-101.
- [7] A. Carlmark, E. Larsson, E. Malmström, Grafting of cellulose by ring-opening polymerisation–A review, Eur. Polym. J. 48 (10) (2012) 1646–1659.
- [8] S. Fujisawa, T. Saito, S. Kimura, T. Iwata, A. Isogai, Surface engineering of ultrafine cellulose nanofibrils toward polymer nanocomposite materials, Biomacromolecules 14 (5) (2013) 1541–1546.
- [9] M. Hakalahti, A. Mautner, L.-S. Johansson, T. Hänninen, H. Setälä, E. Kontturi, A. Bismarck, T. Tammelin, Direct interfacial modification of nanocellulose films for thermoresponsive membrane templates, ACS Appl. Mater. Interfaces 8 (5) (2016) 2923–2927.
- [10] H. Orelma, L.-S. Johansson, I. Filpponen, O.J. Rojas, J. Laine, Generic Method for Attaching Biomolecules via Avidin-Biotin Complexes Immobilized on Films of Regenerated and Nanofibrillar Cellulose, Biomacromolecules 13 (9) (2012) 2802–2810.
- [11] M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, Spontaneously organized molecular assemblies. 4. Structural characterization of n-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy, and electrochemistry, J. Am. Chem. Soc. 109 (12) (1987) 3559–3568.
- [12] R.G. Nuzzo, D.L. Allara, Adsorption of bifunctional organic disulfides on gold surfaces, J. Am. Chem. Soc. 105 (13) (1983) 4481–4483.
- [13] H. Sellers, A. Ulman, Y. Shnidman, J.E. Eilers, Structure and binding of alkanethiolates on gold and silver surfaces: implications for self-assembled monolayers, J. Am. Chem. Soc. 115 (21) (1993) 9389–9401.
- [14] T.J. Deming, Mussel byssus and biomolecular materials, Curr. Opin. Chem. Biol. 3 (1) (1999) 100–105.
- [15] G. Guerrero, P.H. Mutin, A. Vioux, Anchoring of phosphonate and phosphinate coupling molecules on titania particles, Chem. Mater. 13 (11) (2001) 4367– 4373.

- [16] Y. Fujii, Z. Yang, J. Leach, H. Atarashi, K. Tanaka, O.K.C. Tsui, Affinity of Polystyrene Films to Hydrogen-Passivated Silicon and Its Relevance to theTgof the Films, Macromolecules 42 (19) (2009) 7418–7422.
- [17] P. Gin, N. Jiang, C. Liang, T. Taniguchi, B. Akgun, S.K. Satija, M.K. Endoh, T. Koga, Revealed architectures of adsorbed polymer chains at solid-polymer melt interfaces, Phys. Rev. Lett. 109 (26) (2012) 265501.
- [18] C. Housmans, M. Sferrazza, S. Napolitano, Kinetics of Irreversible Chain Adsorption, Macromolecules 47 (10) (2014) 3390–3393.
- [19] N. Jiang, J. Shang, X. Di, M.K. Endoh, T. Koga, Formation Mechanism of High-Density, Flattened Polymer Nanolayers Adsorbed on Planar Solids, Macromolecules 47 (8) (2014) 2682–2689.
- [20] S. Napolitano, S. Capponi, B. Vanroy, Glassy dynamics of soft matter under 1D confinement: how irreversible adsorption affects molecular packing, mobility gradients and orientational polarization in thin films, Eur. Phys. J. E 36 (6) (2013) 61.
- [21] S. Napolitano, A. Pilleri, P. Rolla, M. Wubbenhorst, Unusual deviations from bulk behavior in ultrathin films of poly (tert-butylstyrene): Can dead layers induce a reduction of T g?, ACS Nano 4 (2) (2010) 841–848
- [22] S. Napolitano, M. Wübbenhorst, The lifetime of the deviations from bulk behaviour in polymers confined at the nanoscale, Nat. Commun. 2 (1) (2011) 1–7.
- [23] Y. Ren, M.S. Shoichet, T.J. McCarthy, S.L. Hsu, Spectroscopic characterization of polymer adsorption at the air-solution interface, Macromolecules 28 (1) (1995) 358-364.
- [24] M.S. Shoichet, T.J. McCarthy, Surface modification of poly (tetrafluoroethyleneco-hexafluoropropylene) film by adsorption of poly (L-lysine) from aqueous solution, Macromolecules 24 (6) (1991) 1441–1442.
- [25] W. Chen, T.J. McCarthy, Layer-by-layer deposition: a tool for polymer surface modification, Macromolecules 30 (1) (1997) 78–86.
- [26] D.R. lyengar, J.V. Brennan, T.J. McCarthy, Spontaneous adsorption of polystyrene from solution to the cyclohexane-poly (vinylidene fluoride) interface, Macromolecules 24 (21) (1991) 5886–5888.
- [27] J.M. Stouffer, T.J. McCarthy, Polymer monolayers prepared by the spontaneous adsorption of sulfur-functionalized polystyrene on gold surfaces, Macromolecules 21 (5) (1988) 1204–1208.
- [28] J. Glass, H. Ahmed, S. Seneker, G. McCarthy, Adsorption of water-soluble polymers on high surface area solids.: I. Factors affecting external and interlayer adsorption in carbohydrate polymers, Colloids Surf. 21 (1986) 323–334.
- [29] K.S. Kontturi, K. Biegaj, A. Mautner, R.T. Woodward, B.P. Wilson, L.-S. Johansson, K.-Y. Lee, J.Y.Y. Heng, A. Bismarck, E. Kontturi, Noncovalent Surface Modification of Cellulose Nanopapers by Adsorption of Polymers from Aprotic Solvents, Langmuir 33 (23) (2017) 5707–5712.
- [30] E. Karabulut, T. Pettersson, M. Ankerfors, L. Wågberg, Adhesive layer-by-layer films of carboxymethylated cellulose nanofibril-dopamine covalent bioconjugates inspired by marine mussel threads, ACS Nano 6 (6) (2012) 4731-4739.
- [31] O. Guiselin, Irreversible adsorption of a concentrated polymer solution, EPL (Europhysics Letters) 17 (3) (1992) 225–230.
- [32] M.F. Thees, J.A. McGuire, C.B. Roth, Review and reproducibility of forming adsorbed layers from solvent washing of melt annealed films, Soft Matter 16 (23) (2020) 5366–5387.
- [33] S. Napolitano, Irreversible adsorption of polymer melts and nanoconfinement effects, Soft Matter 16 (23) (2020) 5348-5365.
- [34] M.J. Burroughs, S. Napolitano, D. Cangialosi, R.D. Priestley, Direct measurement of glass transition temperature in exposed and buried adsorbed polymer nanolayers, Macromolecules 49 (12) (2016) 4647–4655.
- [35] H. Yin, S. Napolitano, A. Schönhals, Molecular mobility and glass transition of thin films of poly (bisphenol a carbonate), Macromolecules 45 (3) (2012) 1652–1662.
- [36] N. Jiang, L. Sendogdular, X. Di, M. Sen, P. Gin, M.K. Endoh, T. Koga, B. Akgun, M. Dimitriou, S. Satija, Effect of CO2 on a mobility gradient of polymer chains near an impenetrable solid, Macromolecules 48 (6) (2015) 1795–1803.
- [37] M.L. Braatz, L. Infantas Melendez, M. Sferrazza, S. Napolitano, Unexpected impact of irreversible adsorption on thermal expansion: Adsorbed layers are not that dead, J. Chem. Phys. 146 (20) (2017) 203304.
- [38] T. Koga, N. Jiang, P. Gin, M. Endoh, S. Narayanan, L. Lurio, S. Sinha, Impact of an irreversibly adsorbed layer on local viscosity of nanoconfined polymer melts, Phys. Rev. Lett. 107 (22) (2011) 225901.
- [39] M. Asada, N. Jiang, L. Sendogdular, P. Gin, Y. Wang, M.K. Endoh, T. Koga, M. Fukuto, D. Schultz, M. Lee, X. Li, J. Wang, M. Kikuchi, A. Takahara, Heterogeneous lamellar structures near the polymer/substrate interface, Macromolecules 45 (17) (2012) 7098–7106.
- [40] D.E. Martínez-Tong, B. Vanroy, M. Wübbenhorst, A. Nogales, S. Napolitano, Crystallization of poly (l-lactide) confined in ultrathin films: competition between finite size effects and irreversible chain adsorption, Macromolecules 47 (7) (2014) 2354–2360.
- [41] N. Jiang, J. Wang, X. Di, J. Cheung, W. Zeng, M.K. Endoh, T. Koga, S.K. Satija, Nanoscale adsorbed structures as a robust approach for tailoring polymer film stability, Soft Matter 12 (6) (2016) 1801–1809.
- [42] N. Jiang, JustinM. Cheung, Y. Guo, M.K. Endoh, T. Koga, G. Yuan, S.K. Satija, Stability of Adsorbed Polystyrene Nanolayers on Silicon Substrates, Macromol. Chem. Phys. 219 (3) (2018) 1700326, https://doi.org/10.1002/macp. v219.310.1002/macp.201700326.
- [43] A. Beena Unni, G. Vignaud, J. Bal, N. Delorme, T. Beuvier, S. Thomas, Y. Grohens, A. Gibaud, Solvent assisted rinsing: Stability/instability of ultrathin polymer residual layer, Macromolecules 49 (5) (2016) 1807–1815.

W. Xu, K. Mihhels, N. Kotov et al.

- [44] J.R. Vig, UV/ozone cleaning of surfaces, J. Vac. Sci. Technol., A 3 (3) (1985) 1027–1034.
- [45] L.S. Johansson, J. Campbell, Reproducible XPS on biopolymers: cellulose studies, Surf. Interface Anal. 36 (8) (2004) 1018–1022.
- [46] L.-S. Johansson, J.M. Campbell, O.J. Rojas, Cellulose as the in situ reference for organic XPS. Why? Because it works, Surf. Interface Anal. 52 (12) (2020) 1134– 1138.
- [47] H.G. Tompkins, A user's guide to ellipsometry, Courier Corporation (2006).
- [48] N. Otsu, A threshold selection method from gray-level histograms, IEEE Transactions on Systems, Man, and Cybernetics 9 (1) (1979) 62–66.
- [49] A.A. Govyadinov, I. Amenabar, F. Huth, P.S. Carney, R. Hillenbrand, Quantitative measurement of local infrared absorption and dielectric function with tipenhanced near-field microscopy, J. Phys. Chem. Lett. 4 (9) (2013) 1526–1531.
- [50] F. Huth, A. Chuvilin, M. Schnell, I. Amenabar, R. Krutokhvostov, S. Lopatin, R. Hillenbrand, Resonant antenna probes for tip-enhanced infrared near-field microscopy, Nano Lett. 13 (3) (2013) 1065–1072.
- [51] N. Ocelic, A. Huber, R. Hillenbrand, Pseudoheterodyne detection for background-free near-field spectroscopy, Appl. Phys. Lett. 89 (10) (2006) 101124, https://doi.org/10.1063/1.2348781.
- [52] D. Nečas, P. Klapetek, Gwyddion: an open-source software for SPM data analysis, Open Physics 10 (1) (2012) 181–188.
- [53] T. Huhtamäki, X. Tian, J.T. Korhonen, R.H.A. Ras, Surface-wetting characterization using contact-angle measurements, Nat. Protoc. 13 (7) (2018) 1521–1538.
- [54] A. Thøgersen, J.H. Selj, E.S. Marstein, Oxidation effects on graded porous silicon anti-reflection coatings, J. Electrochem. Soc. 159 (5) (2012) D276–D281.
- [55] G. Beamson, D. Briggs, High resolution XPS of organic polymers, the scienta ESCA300 database, Wiley, Chichester, 1992, p. 295.
- [56] S. Tougaard, Accuracy of the non-destructive surface nanostructure quantification technique based on analysis of the XPS or AES peak shape, Surf. Interface Anal. 26 (4) (1998) 249–269.
- [57] J.S. Johannessen, W.E. Spicer, Y.E. Strausser, An Auger analysis of the SiO2-Si interface, J. Appl. Phys. 47 (7) (1976) 3028–3037.
- [58] C. Bollinne, S. Cuenot, B. Nysten, A.M. Jonas, Spinodal-like dewetting of thermodynamically-stable thin polymer films, Eur. Phys. J. E 12 (3) (2003) 389–396.
- [59] R. Seemann, S. Herminghaus, K. Jacobs, Gaining control of pattern formation of dewetting liquid films, J. Phys.: Condens. Matter 13 (21) (2001) 4925–4938.
- [60] Y. Xia, E. Kim, X.-M. Zhao, J.A. Rogers, M. Prentiss, G.M. Whitesides, Complex optical surfaces formed by replica molding against elastomeric masters, Science 273 (5273) (1996) 347–349.
- [61] D.N. Simavilla, W. Huang, P. Vandestrick, J.-P. Ryckaert, M. Sferrazza, S. Napolitano, Mechanisms of Polymer Adsorption onto Solid Substrates, ACS Macro Lett. 6 (9) (2017) 975–979.
- [62] J.K. Bal, T. Beuvier, A.B. Unni, E.A. Chavez Panduro, G. Vignaud, N. Delorme, M.S. Chebil, Y. Grohens, A. Gibaud, Stability of polymer ultrathin films (< 7 nm) made by a top-down approach, ACS Nano 9 (8) (2015) 8184–8193.
- [63] C. Ligoure, L. Leibler, Thermodynamics and kinetics of grafting endfunctionalized polymers to an interface, J. Phys. 51 (12) (1990) 1313–1328.
- [64] C. Housmans, P. Vandestrick, M. Sferrazza, J.-P. Ryckaert, S. Napolitano, Kinetics of Irreversible Adsorption of Polymer Melts onto Solid Substrates, in: S. Napolitano (Ed.), Non-equilibrium Phenomena in Confined Soft Matter, Springer, Cham, 2015, pp. 111–128.
 [65] E. Raphael, P.G. De Gennes, Rubber-rubber adhesion with connector
- [65] E. Raphael, P.G. De Gennes, Rubber-rubber adhesion with connector molecules, J. Phys. Chem. 96 (10) (1992) 4002–4007.
- [66] G. Reiter, J. Schultz, P. Auroy, L. Auvray, Improving adhesion via connector polymers to stabilize non-wetting liquid films, EPL (Europhysics Letters) 33 (1) (1996) 29–34.
- [67] G. Reiter, P. Auroy, L. Auvray, Instabilities of thin polymer films on layers of chemically identical grafted molecules, Macromolecules 29 (6) (1996) 2150– 2157.
- [68] D. Kurouski, A. Dazzi, R. Zenobi, A. Centrone, Infrared and Raman chemical imaging and spectroscopy at the nanoscale, Chem. Soc. Rev. 49 (11) (2020) 3315–3347.

- [69] L. Mester, A.A. Govyadinov, S. Chen, M. Goikoetxea, R. Hillenbrand, Subsurface chemical nanoidentification by nano-FTIR spectroscopy, Nat. Commun. 11 (1) (2020) 1–10.
- [70] M. Meyns, S. Primpke, G. Gerdts, Library based identification and characterisation of polymers with nano-FTIR and IR-sSNOM imaging, Anal. Methods 11 (40) (2019) 5195–5202.
- [71] M.R. Jung, F.D. Horgen, S.V. Orski, V. Rodriguez C., K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.-J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, Mar. Pollut. Bull. 127 (2018) 704–716.
- [72] M.J.B. Davis, K. Randazzo, B. Zuo, R.D. Priestley, Revealing Interfacial Interactions in Random Copolymer Adsorbed Layers by Solvent Leaching, Macromol. Rapid Commun. 41 (6) (2020) 1900582, https://doi.org/ 10.1002/marc.v41.610.1002/marc.201900582.
- [73] R. Seemann, S. Herminghaus, K. Jacobs, Dewetting patterns and molecular forces: a reconciliation, Phys. Rev. Lett. 86 (24) (2001) 5534–5537.
- [74] G. Reiter, R. Khanna, A. Sharma, Enhanced instability in thin liquid films by improved compatibility, Phys. Rev. Lett. 85 (7) (2000) 1432–1435.
- [75] H. Zhao, Y.J. Wang, O.K.C. Tsui, Dewetting induced by complete versus nonretarded van der Waals forces, Langmuir 21 (13) (2005) 5817–5824.
- [76] G. Reiter, M. Hamieh, P. Damman, S. Sclavons, S. Gabriele, T. Vilmin, E. Raphaël, Residual stresses in thin polymer films cause rupture and dominate early stages of dewetting, Nat. Mater. 4 (10) (2005) 754–758.
- [77] X.u. Li, X. Lu, Interfacial Irreversibly and Loosely Adsorbed Layers Abide by Different Evolution Dynamics, ACS Macro Lett. 8 (11) (2019) 1426–1431.
- [78] X.u. Li, X. Lu, Evolution of Irreversibly Adsorbed Layer Promotes Dewetting of Polystyrene Film on Sapphire, Macromolecules 51 (17) (2018) 6653–6660.
- [79] K. Brebner, R. Chahal, L. St-Pierre, Adsorption of poly (dimethyl siloxanes) from solution on silica: 1, Polymer 21 (5) (1980) 533–540.
 [80] E. Niinivaara, E. Kontturi, 2D dendritic fractal patterns from an amphiphilic
- polysaccharide, Soft Matter 10 (11) (2014) 1801–1805.
- [81] C.W. Extrand, Contact angles and hysteresis on surfaces with chemically heterogeneous islands, Langmuir 19 (9) (2003) 3793–3796.
- [82] Y. Li, J.Q. Pham, K.P. Johnston, P.F. Green, Contact angle of water on polystyrene thin films: Effects of CO₂ environment and film thickness, Langmuir 23 (19) (2007) 9785–9793.
- [83] C. Vericat, M.E. Vela, G. Corthey, E. Pensa, E. Cortés, M.H. Fonticelli, F. Ibañez, G. E. Benitez, P. Carro, R.C. Salvarezza, Self-assembled monolayers of thiolates on metals: a review article on sulfur-metal chemistry and surface structures, RSC Adv. 4 (53) (2014) 27730–27754.
- [84] K.S. Siow, L. Britcher, S. Kumar, H.J. Griesser, Plasma Methods for the Generation of Chemically Reactive Surfaces for Biomolecule Immobilization and Cell Colonization - A Review, Plasma Processes Polym. 3 (6-7) (2006) 392– 418.
- [85] Y. Mouhamad, P. Mokarian-Tabari, N. Clarke, R.A.L. Jones, M. Geoghegan, Dynamics of polymer film formation during spin coating, J. Appl. Phys. 116 (12) (2014) 123513, https://doi.org/10.1063/1.4896674.
- [86] L. Sun, G. Yuan, L. Gao, J. Yang, M. Chhowalla, M.H. Gharahcheshmeh, K.K. Gleason, Y.S. Choi, B.H. Hong, Z. Liu, Chemical vapour deposition, Nature Review Methods Primers 1 (2021) 5.
- [87] K. Ariga, Y. Yamauchi, T. Mori, J.P. Hill, 25th Anniversary Article: What Can Be Done with the Langmuir-Blodgett Method? Recent Developments and its Critical Role in Materials Science, Adv. Mater. 25 (45) (2013) 6477–6512.
- [88] J.J. Richardson, J. Cui, M. Björnmalm, J.A. Braunger, H. Ejima, F. Caruso, Innovation in Layer-by-Layer Assembly, Chem. Rev. 116 (23) (2016) 14828– 14867.
- [89] A. Cassie, S. Baxter, Wettability of porous surfaces, Trans. Faraday Soc. 40 (1944) 546–551.
- [90] R. Woracek, D. Penumadu, N. Kardjilov, A. Hilger, M. Boin, J. Banhart, I. Manke, Neutron Bragg edge tomography for phase mapping, Physics Procedia 69 (2015) 227–236.