Tomás E. Benavidez
Carlos D. Garcia

Department of Chemistry,
Clemson University, Clemson,
SC, USA

Research Article

Spectroscopic ellipsometry as a complementary tool to characterize coatings on PDMS for CE applications

This paper describes the use of spectroscopic ellipsometry to investigate the adsorption process of model polyelectrolytes (PDDAC and PSS) to thin-films of PDMS. A description of the information collected by ellipsometry as well as complementary information obtained by atomic force microscopy and contact angle measurements is discussed. Upon identification of the driving forces and optimum experimental conditions required for the adsorption, multilayer constructs were fabricated (ranging from 1 to 20 nm in thickness) and used to evaluate their effect on the separation of phenolic compounds by capillary electrophoresis. According to the presented results, polyelectrolyte layers of approximately 10 nm thick provided the best conditions for the separation of the selected phenolic compounds.

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1 Introduction

Manipulating the electro-osmotic flow (EOF) by controlling the chemistry of the capillary surface [1–3] is one of the simplest avenues to optimize the separation process [4, 5]. This is particularly important for the development of microfluidic devices, where much shorter channels are typically used. In addition, a large fraction of these devices are now fabricated in polymeric materials [6,7], and typically suffer some limitations in performance when compared to traditional substrates such as glass. Among them, poly(dimethylsiloxane) (PDMS) is one of the most popular polymers to develop microfluidic devices. PDMS is optically transparent, chemically inert, nontoxic, amenable to low-cost fabrication techniques, compatible with water (as well as a number of solvents) and permeable to most gases, including oxygen [8, 9]. The most important disadvantages of PDMS are its hydrophobicity (contact angle ~110°) and porosity, allowing absorption and adsorption of a wide variety of molecules and thus resulting in unstable migration times, peak tailing, and low separation efficiencies. In order to overcome the aforementioned drawbacks linked to PDMS, a variety of surface modifications have been

proposed [10–15]. Besides covalent modifications, dynamic coatings with surfactants and polyelectrolytes are convenient alternatives because they can be spontaneously deposited on PDMS by simple adsorption without the use of complex instrumentation, chemical modification of the surface, or specific skills. Additionally, polyelectrolytes of different charges (polycations and polyanions) can be sequentially deposited to form multilayers that can mask the underlying substrate and therefore regulate the μ_{EOF} [16, 17], reduce analyte-wall interactions [18], and improve reproducibility [19], solvent resistance [20], and resolution [21]. In other cases, these coatings can be designed to play a more active role in the separation [22, 23].

While the kinetic and thermodynamic aspects of the adsorption of polyelectrolytes to silica are relatively well-understood [24–26], reports describing such interactions with PDMS are much more limited. This gap in knowledge significantly hinders the rational design of analytical strategies based on the application of polyelectrolytes as coating materials for PDMS microchannels. To address this problem, demonstrate the utility of spectroscopic ellipsometry to gain insights about the coating process, and aid in the optimization of CE separations, this manuscript first describes the synthesis and characterization of thin (< 1 nm) layers of PDMS. These films, which exhibit most of the properties of commercial PDMS (e.g. Sylgard 184) [27], were then used as substrates to investigate the adsorption of selected polyelectrolytes under either batch (immersing the substrate in a solution

Correspondence: Carlos D. Garcia, Department of Chemistry, Clemson University, 219 Hunter Laboratories, Clemson, SC 29364, USA
E-mail: cdgarci@clemson.edu
Fax: +1-01 (864) 656-6613

containing the selected polyelectrolyte) or stagnation-point flow conditions [28, 29]. Upon identifying the conditions and time to form well-defined layers of polyelectrolytes on PDMS, the effect of layer thickness was investigated on the electrophoretic separation of a group of phenolic compounds with environmental relevance.

2 Materials and methods

2.1 Reagents and solutions

All chemicals were of analytical grade and used as received. H_2O_2, H_2SO_4, and NaOH were purchased from Fisher Scientific (Pittsburgh, PA). Chlorine-terminated poly(dimethylsiloxane) (PDMS-Cl), dichloromethane (DCM), poly(diallyldimethyl ammonium chloride) (PDDAC, average MW = 200–350 kDa), poly(styrene-4-sodium sulfate) (PSS, average MW = 1000 kDa), phenol (Ph), ferulic acid (*trans*-4-hydroxy-3-methoxycinnamic acid, FA), 2-nitrophenol (2-NP), 2,4-dinitrophenol (2,4-DNP), benzoic acid (BA), and salicylic acid (SA) were purchased from Sigma-Aldrich (Saint Louis, MO). Vanillic acid (VA) and 4-hydroxybenzoic acid (HBA) were obtained from Fluka (Buchs, Germany). All aqueous solutions were prepared using 18 MΩ·cm water (NANOpure Diamond, Barnstead; Dubuque, IA). The pH of the solutions was measured using a glass electrode and digital pH meter (Orion 420A+, Thermo; Waltham, MA) and adjusted using either 1 M NaOH or 1 M HCl. Unless otherwise stated, adsorption of polyelectrolytes was performed with solutions of constant ionic strength, prepared in 10 mM phosphate buffer + 100 mM NaCl (pH = 7.00). Stock solutions (~4–0.3 mM) of phenols were prepared in 10 mM phosphate buffer at pH = 7 and stored at 4°C until use. All experiments were conducted at room temperature.

2.2 Synthesis of PDMS Films

Standard <111> 125 mm silicon wafers (MEMC, Malaysia) were used as substrates because they provide a reflective surface and are coated with a native layer (1.56 ± 0.06 nm) of silica that mimics the material used in capillaries for CE experiments. Initially, the substrates were scored into pieces of 1 cm x 3 cm using a computer-controlled engraver (Gravograph IS400, Gravotech; Duluth, GA). Each piece was then cleaned by immersion in piranha solution (1:3 ratio of H_2O_2:H_2SO_4) at 90°C for 30 min. Next, the substrates were thoroughly rinsed with ultrapure water, 2-propanol, and dried under N_2. The Si/SiO_2 substrates were immersed in a solution containing 2.5% v/v PDMS-Cl (dissolved in dichloromethane) for 1 h, under gentle agitation (40 rpm; MaxQ416 HP; Thermo Scientific). Under the selected conditions, the attachment reaction proceeds rather quickly, leading to the deposition of a layer of PDMS covalently linked to the substrate by a head-to-surface arrangement [30, 31]. The PDMS-coated wafers were rinsed with dichloromethane

to remove any unbound molecules, dried under N_2, and used within 24 h. In contrast with previously reported procedures [27, 32–36], this simple strategy allowed the formation of uniform layers of PDMS with well-defined thickness and minimum roughness. The formation of the PDMS layer was verified by ellipsometry (*vide infra*) at an incident angle of 70° (with respect to the substrate) and with a range of wavelengths between 250 and 800 nm. It is also important to note that other procedures to fabricate PDMS films have been reported [27], but rendered rather heterogeneous films that were not compatible with the ellipsometric analysis.

2.3 Spectroscopic ellipsometry

All ellipsometry experiments described in this manuscript were performed using a variable angle spectroscopic ellipsometer (WVASE, J.A.Woollam Co.; Lincoln, NE) and modeled using the WVASE software package (J.A. Woollam Co., Lincoln, NE). The difference between the experimental and model-generated data was assessed by a built-in function in WVASE (mean square error, MSE) that considers the number of data points used in the measurements, the number of parameters varied in the regression analysis, and the standard deviation of the experimental data. In agreement with literature reports [9], MSE values less than 15 are considered to accurately represent the properties of the substrate. In order to investigate the kinetic aspects of the interaction of polyelectrolytes with PDMS (and determine the adequate time to coat the surface), dynamic adsorption experiments were performed. In such cases, the substrate was placed in a commercial liquid cell (J.A. Woollam Co.; Lincoln,NE) which was mounted on the vertical base of the ellipsometer. As described elsewhere [29, 37], an L-shaped stainless-steel tube was attached to the cell. One end of the tube faced the substrate at the same spot where the incident light beam hits the surface. The other end of the tube was connected to a peristaltic pump (Minipuls3, Gilson; Middleton, WI) using Tygon tubing. A two-way valve (V100D, Upchurch Scientific; Oak Arbor, WA) was also connected in series to enable rapid switching between the background electrolyte and the solution containing the selected polyelectrolyte. In all cases, a spectroscopic scan in 10 nm steps (250 to 800 nm range) was performed using background electrolyte as the ambient medium to determine the thickness of the PDMS substrate. This spectroscopic scan allows calculating the optical properties of the substrate, greatly facilitating the calculation of the thickness of the subsequent layer. The dynamic experiment was then started by pumping buffer to establish the baseline (for ~10 min). Next, the buffer solution containing the selected polyelectrolyte was introduced in the cell and the kinetics of the adsorption process were monitored at 500 nm, allowing data collection at a frequency of 5 Hz. After stable values of the ellipsometric angles were obtained, another spectroscopic scan was performed to more accurately determine the thickness of the deposited layer of polyelectrolyte.

2.4 Surface characterization

In order to evaluate the effect of polyelectrolytes on the surface tension of the PDMS layers, contact angle measurements were performed using a VCA-Optima surface analysis system (Ast Products, Inc.; Billerica, MA) and analyzed using the software provided by the manufacturer, 30 s after dispensing 2 µL of buffer (10 mM phosphate + 100 mM NaCl, pH = 7.00). Atomic force microscopy (AFM) images were obtained using a Veeco diMultiMode Nanoscope V scanning probe microscope operating in tapping and non-contact mode. The samples were analyzed using the software NanoScope v7.30.

2.5 Capillary electrophoresis

In order to take advantage of the autosampling and temperature control capabilities, all CE experiments were performed in an SCIEX P/ACE™ MDQ *plus* capillary electrophoresis system (Framingham, MA) using 50 µm i.d. x 360 µm o.d. x 30.5 cm long fused silica capillaries (Polymicro Technologies; Phoenix, AZ). These capillaries were coated with PDMS using a procedure similar to the one used to modify Si/SiO$_2$ wafers. Briefly, capillaries were first preconditioned by sequentially rinsing them with 1 M NaOH for 4 min and then with ultrapure water for 10 min. After that, capillaries were dried with air (10 min) and rinsed with DCM for 5 min. For the modification, capillaries were flushed with a PDMS-Cl solution (2.5% v/v in DCM) during 1 h. Then, the capillaries were sequentially rinsed with DCM (10 min), methanol (10 min), and ultrapure water (10 min). Before performing the CE experiments, the SiO$_2$/PDMS capillaries were preconditioned by a rinsing step with phosphate buffer (5 min, 20 psi). Data acquisition and analysis were performed using 32 Karat software, version 10.2.9 (AB SCIEX). Samples were hydrodynamically injected by applying 0.5 psi for 4 s. CE separation was carried out applying +15 kV at 25°C. Direct UV detection was achieved using a wavelength of 214 nm through a capillary window located 20.5 cm from the inlet.

3 Results and discussion

3.1 Characterization of the PDMS Films

As previously stated, Si/SiO$_2$ wafers were initially coated with a thin layer of covalently-bound PDMS by the reaction between the SiOH groups on the surface of the wafer and the chloro-group in the siloxane. This reaction was selected because it is fast, simple, and proceeds in one step with the release of hydrochloric acid [30, 38]. The resulting Si/SiO$_2$/PDMS substrates were then characterized by SE, contact angle measurements, and AFM.

In order to determine the kinetics of the coating process ($\Delta d/dt$) and calculate the resulting thickness (d), an optical model describing the properties of the substrates in terms of optical constants (refractive index, n, and extinction coef-

ficient, k) and thickness was used. In the present study, the model used to represent the optical properties of the substrates was composed of a layer of Si (bulk; $d = 1$ mm), a layer of SiO$_2$ ($d = 1.56 \pm 0.06$ nm), and a transparent layer of PDMS represented by a Cauchy function. Figure 1A shows the results of a spectroscopic scan (dependence of Ψ and Δ as a function of wavelength) obtained at an angle of incidence of 70° for a representative film of PDMS deposited on a Si/SiO$_2$ wafer. As it can be observed, a good agreement (MSE = 2.98) between the experimental (data points) and the model-generated data (lines) was obtained. This agreement indicates that the proposed model can be used to calculate the thickness of the resulting substrates (0.68 $\pm$ 0.05 nm, $n = 17$), which were considered adequate for the objectives of this project. The optical constants, calculated from these experiments (data not shown), were in good agreement with previously reported values for PDMS prepared by other methods [9, 39].

Using this information as the starting point, the parameters of an additional Cauchy layer (representing the adsorbed polyelectrolytes) were then calculated and used to determine the adsorbed amount (Γ, expressed in mg/m^2) using Eq. (1),

$$\Gamma = \frac{d(n - n_0)}{(dn/dc)} \tag{1}$$

where n and n_0 are the refractive indexes of the polyelectrolyte ($n = 1.54$ for PDDAC and PSS) [25] and the ambient ($n_0 = 1.3333$ for H$_2$O), respectively. In accordance with previous reports [40], the refractive index increment for the molecules in the layer (dn/dc) was considered to be 0.170 g/mL [41].

Contact angle measurements were also obtained to gain insight on the hydrophobicity of the films. The results (112 $\pm$ 1°, $n = 3$) indicate that the Si/SiO$_2$/PDMS substrates are rather hydrophobic and that the values are within the range of previously reported values for commercial PDMS [9, 27, 42]. Additionally, the topography of the substrates was investigated by atomic force microscopy (AFM). As shown in Fig. 1B, a uniform coverage was obtained with an average surface roughness of 0.04 nm. Therefore, the presented results provide evidence that the selected reaction conditions allow the deposition of thin-films of a material that has the same siloxane backbone (which dictates the elasticity of the polymer) [43], the same methyl side groups (which dictate the hydrophobicity) [44], similar contact angle, and similar topography as commercial PDMS (e.g. Sylgard 184) [45, 46]. Additionally, these films are also similar to those prepared by the reaction of tetra-(dimethylsiloxane) [9], which was proposed to form PDMS-like films. In order to verify that changes in thickness were attributed only to the adsorption of polyelectrolytes and not to peeling or swelling of the PDMS substrate, the stability of the PDMS layer in buffer solution was investigated as a function of time. The results (*vide infra*, Fig. 2A) indicate that the selected background electrolyte did not induce significant changes in thickness, therefore, allowing the use of the proposed substrates to model PDMS for the adsorption and subsequent CE experiments.
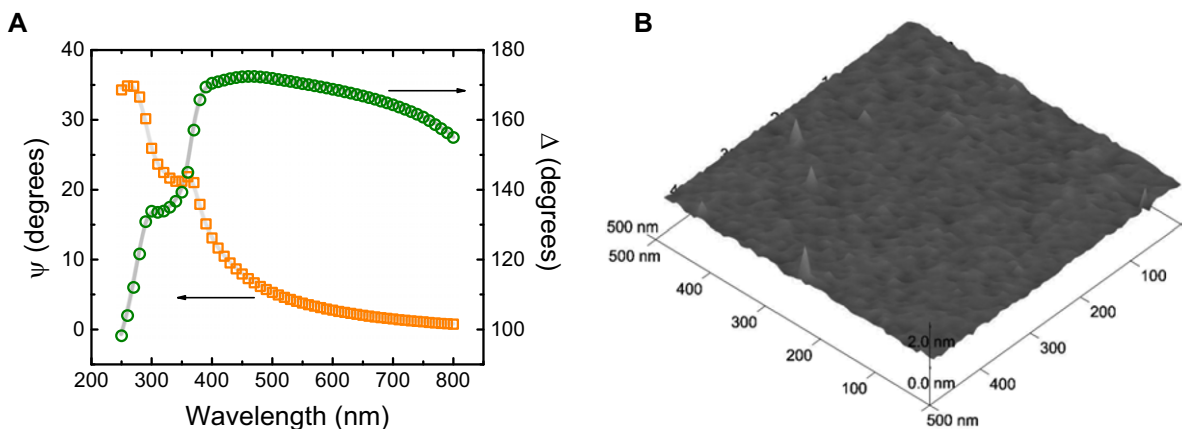
Figure 1. (A) Spectroscopic scan of PDMS layer (0.68 ± 0.05 nm) on Si/SiO2 in the 250–800 nm range. Experimental (points) and model-generated data (line). (B) AFM image of the Si/SiO$_2$ surface upon modification with PDMS.
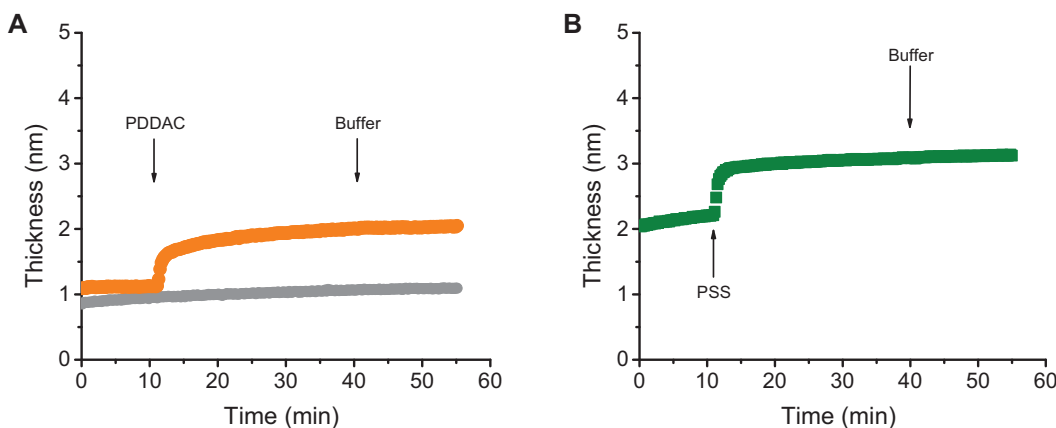
Figure 2. (A) Baseline obtained for a PDMS layer (■) and dynamic adsorption of 0.100 mg/mL PDDAC to PDMS (■). (B) Dynamic adsorption of 0.100 mg/mL PSS onto PDMS/PDDAC surface. Experimental conditions as described in the experimental section

3.2 Adsorption of polyelectrolytes to PDMS

Two model polyelectrolytes were selected for the present studies: poly(diallyldimethyl ammonium chloride) (PDDAC) and poly(styrene-4-sodium sulfate) (PSS) [47]. Although layers (and multilayers) of these polyelectrolytes have been extensively used in silica-based CE separations [18, 19, 48], limited information is available related to the thickness or the kinetic aspects of their interaction with PDMS. Initially, the adsorption of PDDAC (polycation) to PDMS was investigated. As shown in Fig. 2A, the adsorption proceeded rather quickly, displaying three distinct phases within each experiment. In the first phase, the adsorbed amount increased linearly with respect to time (determining the initial adsorption rate), followed by a second phase during which the adsorption rate gradually decreased, reaching a third phase (∼30 min) where the adsorbed amount approaches a constant value (determining the Γ_{SAT}). As it can also be observed in Fig. 2A, no PDDAC desorption was observed upon rinsing the coated surface with background electrolyte, in agreement with previous reports that considered the adsorption of PDDAC to be driven by

electrostatic interactions and results in a process that is (effectively) irreversible [25]. This adsorption results in changes in entropy (release of water molecules and ions) [49] and is therefore more affected by the concentration of ions in the background electrolyte than by the concentration of polyelectrolyte [25]. These observations also explain why lower amounts of PDDAC are adsorbed to the slightly negative surface of the PDMS (in comparison to the amount adsorbed to silica surfaces [50–52]), yielding positively charged with enhanced hydrophilic properties (contact angle 67.0 ± 0.2°, $n = 3$). Moreover, the electrostatic nature of the interaction can be also used to explain why no significant adsorption was observed when PSS was exposed to bare PDMS (data not shown).

A major challenge in CE, particularly when PDMS channels are used, is the ability to control the direction, magnitude, and stability of the EOF. One way to address these issues is by the successive adsorption of layers of polycations and polyanions [53]. Therefore, the adsorption of PSS to a film of PDMS coated with a layer of the polycation (PDMS/PDDAC) was investigated. As shown in Fig. 2B, the adsorption of

Table 1. Summary of the results obtained for the dynamic adsorption experiments of polyelectrolytes, as determined by spectroscopic ellipsometry

[Polyelectrolyte] (mg/mL)		Initial growth rate (nm/min)	Thickness (nm)	t_{95} (min)	Γ_{SAT} (mg/m^2)
PDDAC on PDMS	0.001	0.0727 ± 0.0008	0.82 ± 0.06	20	0.62 ± 0.05
	0.010	0.250 ± 0.008	0.84 ± 0.07	10	0.63 ± 0.05
	0.100	0.60 ± 0.03	1.09 ± 0.05	5	0.82 ± 0.04
PSS on PDMS/PDDAC	0.001	0.0314 ± 0.0004	0.69 ± 0.05	18	0.52 ± 0.04
	0.010	0.326 ± 0.009	0.93 ± 0.05	6	0.70 ± 0.04
	0.100	1.03 ± 0.02	1.14 ± 0.05	3	0.86 ± 0.04

0.100 mg/mL PSS also displays the three distinct phases described for the adsorption of PDDAC, but proceeds much faster than the first layer of PDDAC. This finding can be attributed to higher charge density of the PDMS/PDDAC surface (in comparison to that of PDMS). A slight baseline drift is also evident in Fig. 2B. This phenomenon, which has been previously reported for other systems involving polyelectrolytes [54–56], was attributed to the stabilization of the PDDAC layer upon rinsing the surface with buffer and was no longer observed upon the adsorption of the first layer of the polyanion.

In order to determine the optimum conditions to coat the surface of PDMS, the effect of the concentration of both polyelectrolytes on the adsorption process was also investigated. As summarized in Table 1, the selected concentration of polyelectrolyte (in the 0.001, 0.010, and 0.100 mg/mL range) had significant effects on the initial adsorption rate, but rendered layers with only slightly different thickness values. Again, these results can be attributed to a process mostly driven by electrostatic interaction of the polyelectrolytes that tend to reach a saturation point once the charges are compensated. As expected, the higher the concentration of polyelectrolytes in the impinging solution, the faster that condition is achieved.

3.3 Thickness of multilayer PDDAC/PSS constructs on PDMS

One of the strategies to mask the hydrophobic nature of PDMS and control peak tailing is to deposit multiple layers of alternating charges (PDDAC/PSS). Although this strategy has proven successful in many CE separations, it is critical to understand the dependency of thickness on the number of layers. In agreement with literature reports [25], preliminary experiments demonstrated (data not shown) that the final thickness of the polyelectrolyte layer is not affected by the hydrodynamic conditions used during the adsorption. In other words, equivalent films were obtained by either impinging a polyelectrolyte solution onto the substrate or by immersion of a substrate in a solution under identical experimental conditions (10 mM phosphate buffer + 100 mM NaCl, pH = 7.00). Therefore, PDMS-coated wafers were sequentially immersed in a solution containing either PDDAC (0.100 mg/mL) or PSS (0.100 mg/mL). In all cases, spectroscopic scans were performed to follow the change in thickness upon the ad-
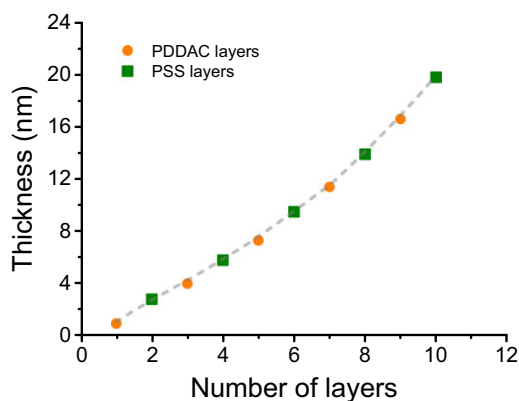
Figure 3. Dependence of thickness on the number of layers adsorbed. Odd and even layer numbers represent layers of the polycation (PDDAC) and polyanion (PSS), respectively. Line included to guide the eye. Error bars contained within the data points.

sorption of each layer. As shown in Fig. 3 the thickness of the resulting construct was found to be dependent on the number of layers and about 1/10 of the values reported when the films were prepared from ethanolic solutions [47]. It is important to note that a slight upward curvature was observed, thus suggesting a growth pattern similar to that of other multilayer systems [57–59], where the formation of intermixed layers is affected by the overcompensation of surface charges with counterions from the background electrolyte [25, 60].

It is also important to mention that according to AFM images (data not shown), the adsorption of multiple layers of polyelectrolytes to PDMS resulted in increases in the roughness of the surface from 0.04 nm (PDMS) to 0.2 nm (one bilayer of PDDAC/PSS) and 1.8 nm (three bilayers of PDDAC/PSS). These increases in roughness, which are less pronounced than those observed in silica surfaces [51–53, [61]], have been attributed to the fuzzy structure of the interpenetrated layers [60] and the reorganization of chains within the bilayer.

3.4 Effect of multilayer PDDAC/PSS constructs on the separation of phenolic compounds by CE

According to the presented results, solutions containing 0.100 mg/mL of the polyelectrolytes are sufficient to saturate the surface with one layer of polyelectrolyte within a few
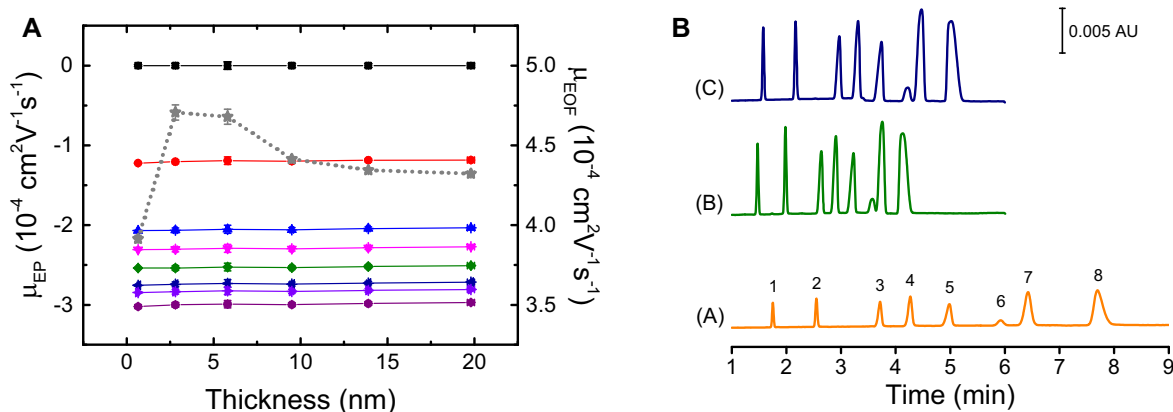
Figure 4A. Effect of the thickness of PDDAC/PSS bilayers adsorbed to the PDMS surface on the electro-osmotic (★) and electrophoretic mobility of phenol (■), 2-nitrophenol (●), ferulic acid (▲), vanillic acid (▼), 4-hydroxybenzoic acid (◆), 2,4-dinitrophenol (◀), benzoic acid (▶), and salicylic acid (⬣). Separation conditions: 10 mM phosphate running buffer, E_{SEP} = 15 kV, detection at 214 nm. Error bars contained within the data points.

Figure 4B. Representative electropherograms obtained with plain PDMS (A) and with a capillary coated with 2 (B) and 5 (C) bilayers of PDDAC/PSS during the separation of phenol (1), 2-nitrophenol (2), ferulic acid (3), vanillic acid (4), 4-hydroxybenzoic acid (5), 2,4-dinitrophenol (6), benzoic acid (7), and salicylic acid (8).

minutes (5 min or less, according to Table 1). If required, the thickness of the multilayer construct can be increased by adsorbing successive layers of polyelectrolytes of alternating charges (PDDAC/PSS), considering that a rinsing step is required between each layer (to avoid forming large aggregates). Such multilayer coatings may provide higher surface coverage, better stability, and pH-independent EOF values [26, 62, 63]. However, they also require longer preparation times and may not necessarily provide the optimum performance for CE separations, as thick layers may behave as stationary phases [64,65]. In order to critically evaluate the effect of polyelectrolyte coatings on the separation, silica capillaries were modified with PDMS and coated with varying thicknesses of polyelectrolytes bilayers (exposing a negatively charged surface to preserve the EOF direction).

Due to their environmental and biomedical relevance [66] as well as their ability to interact with hydrophobic materials (such as PDMS) [16, 27, 67, 68], a group of eight phenolic compounds was selected for these experiments. These compounds (phenol, 2-nitrophenol, 2,4-dinitrophenol, ferulic acid, benzoic acid, salicylic acid, vanillic acid and 4-hydroxybenzoic acid) are used in many industrial activities and can be released to ecosystems by the natural degradation of organic matter. As they can accumulate in these ecosystems, their concentration in water samples should be carefully monitored.

As it can be observed in Fig. 4A, capillaries coated with a layer of PDMS rendered a rather long analysis time (8.5 min) and low EOF values ($3.91 \pm 0.02 \times 10^{-4}$ cm$^2 \cdot$V$^{-1} \cdot$s^{-1}). Upon modification with the first bilayer of polyelectrolytes, a significant increase in the EOF ($4.7 \pm 0.5 \times 10^{-4}$ cm$^2 \cdot$V$^{-1} \cdot$s^{-1}) and the corresponding decrease in analysis time were observed. Subsequent bilayers produced slight decreases in the EOF, reaching a plateau when the capillary was coated with a polyelectrolyte layer of 13.9 ± 0.1 nm (4 bilayers, $4.34 \pm$

0.01×10^{-4} cm$^2 \cdot$V$^{-1} \cdot$s^{-1}). These changes in EOF (attributed to the differences in charge density over the capillary surface) were accompanied by changes in peak width, specially noted for the phenolic compounds featuring the lowest mobilities (2NP, BA, and SA). In general, it can be observed that while the peak shape was significantly improved when the capillary was coated with two to three bilayers of polyelectrolytes, sequential increases in peak skew and peak width were obtained thereafter (as shown in Fig. 4B). For the case of SA (peak #8 in Fig. 4B), the peak skew (Fisher skewness) changed from 0.62 (PDMS), to 0.38 (two bilayers), to 0.48 (five bilayers). More information regarding the parameters obtained for the separation (peak area, peak width, t_M, and N) is available as Supplementary Information. These differences were attributed to increased analyte-wall interactions and surface roughness. As a representative examples, Fig. 4B shows electropherograms obtained with a capillary modified with bare PDMS, with two bilayers of PDDAC/PSS (5.8 ± 0.1 nm), and with five bilayers of PDDAC/PSS (19.8 ± 0.2 nm).

4   Concluding remarks

In agreement with literature reports performed on silica surfaces, the adsorption of polyelectrolytes to PDMS is a fast, electrostatically-driven process ocurring *via* overcompensation of surface charges, and resulting in the deposition of thin layers, with roughness values in the sub-nm range. These results are somewhat counterintuitive, as hydrophobic interactions dominate the adsorption and absorption of a wide variety of other molecules to PDMS. Under the selected conditions, the concentration of polyelectrolyte had significant effects on the initial adsorption rate, but rendered layers with only slightly different thickness values. When compared to experiments performed in silica, lower adsorbed amounts

were obtained in the selected PDMS surfaces, translating in thicknesses of about 2 nm per PDDAC/PSS, value that grows (almost) proportionally with the number of bilayers deposited. While the formation of the first layer of PDDAC requires about 20 min, subsequent layers only require a few minutes. When applied to electrophoretic separations, PDDAC/PSS layers allow controlling the μ_{EOF} and decreasing analyte-wall interactions. The best separation was obtained when two to three bilayers of PDDAC/PSS were adsorbed (depending on the criteria used), rendering thickness values for the coating of <10 nm. Although plenty of information related to the effect of polyelectrolytes in CE separations is currently available, the thickness of the coatings deposited on PDMS, as well as the corresponding performance, can be significantly affected by a number of experimental variables, therefore highlighting the importance of using complementary instrumentation to support the separation process.

Authors declare no conflict of interest.

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