# Chapter 4: Adsorbed Layer Thickness Determination Streaming Potential Experiments

## 4.1. Goal

The adsorption isotherms experiments described in Chapter 3 provide information on the amount of polymer adsorbed on a metal oxide surface. Adsorption isotherm experiments do not, however, provide any information as to the thickness of the polymer layer. The amount of polymer and the thickness of the adsorbed polymer layer are important parameters which must be determined in order to design a polymer for use as a nonionic steric stabilizer of metal oxide particles in aqueous media. The objectives of the research in this chapter was to construct a streaming potential apparatus and use it to measure the adsorbed layer thickness of homopolymer anchor blocks that adsorb on SiO<sub>2</sub>. This information is necessary for characterizing the behavior of nonionic anchor blocks, and will also provide valuable measurements of the adsorbed layer thickness of nonionic block copolymers designed to form brush-like layers.

#### 4.2. Background

When two phases are in contact with one another, there is usually a potential difference between them. When this difference arises due to tangential flow of one phase past the other, the resulting effects are termed electrokinetic. Adsorption of an uncharged polymer on a charged capillary surface has been observed to alter the electrokinetic properties of the capillary due to the polymer promoting changes in the tangential flow of fluid along the surface. In many cases, the zeta potential,  $\zeta$ , is reduced and this reduction is interpreted as an outward displacement of the shear plane.<sup>1-5</sup> Thus, electrokinetic techniques, such as electrophoresis or streaming potential, have been used to measure the adsorption of nonionic polymers in aqueous media, and calculate the resulting electrokinetic layer thickness,  $\delta_e$ , a measure of the location of the shear plane, from the relationship

$$\tanh\left(\frac{ze\,\zeta}{4kT}\right) = \tanh\left(\frac{ze\,\zeta}{4kT}\right)\exp\left(-\kappa\delta_{e}\right) \qquad [4.2.1]$$

where  $\zeta$  is the zeta potential of the flow channel when polymer is adsorbed,  $\zeta_0$  is the zeta potential of the flow channel without adsorbed polymer, z is the valence of the added electrolyte, e is the electronic charge, and  $\kappa^{-1}$  is the Debye length.<sup>4</sup> As stated, equation [4.1.1] is not useful, but for low values of  $\zeta$ ,  $\zeta \leq 50$  mV, it may be rearranged to give<sup>4</sup>

$$\delta_{\rm e} = \kappa^{-1} \ln(\zeta/\zeta_{\rm o}) \qquad [4.2.2]$$

 $\zeta$  and  $\zeta_0$  may be related to their respective streaming potentials as

$$\zeta = 1.055 \times 10^5 \frac{V_s}{P} (\lambda_0 + \frac{2\lambda_s}{r})$$
[4.2.3]

$$\zeta_0 = 1.055 x 10^5 \frac{V_{so}}{P} (\lambda_0 + \frac{2\lambda_s}{r})$$
 [4.2.4]

where  $V_{SO}$  is the streaming potential for the buffer solution, and  $V_S$  is the streaming potential measured for the buffer containing a nonionic polymer, P is the pressure in cm of Hg, r is the capillary radius in cm,  $\lambda_0$  is the electrical conductivity in ohm<sup>-1</sup>cm<sup>-1</sup>,  $\lambda_s$  is the specific surface conductivity in ohm<sup>-1</sup>.  $\zeta$ ,  $\zeta_0$ ,  $V_{SO}$ , and  $V_S$  all have the same units, typically mV.<sup>1</sup> Thus, the defining relationship for electrostatic layer thickness in terms of the streaming potential results from substitution of equations [4.2.3] and [4.2.4] into equation [4.2.2]

$$\delta_{\rm e} = \kappa^{-1} \ln(V_{\rm SO}/V_{\rm S}) \qquad [4.2.5]$$

 $\delta_e$  has been shown to be dependent on the ionic strength of the buffer solution, and approaches a limiting maximum value of  $\delta_H$ , the hydrodynamic layer thickness, at dilute ionic strengths, commonly 10<sup>-3</sup> or 10<sup>-4</sup> M NaCl.<sup>4</sup> Thus, equation [4.2.5] may be rewritten

$$\delta_{\rm H} = \kappa^{-1} \ln(V_{\rm so}/V_{\rm s}) \qquad [4.2.6]$$

Hereafter, the subscript, H, will be dropped, and it will be understood that  $\delta$  is  $\delta_{H}$ . This method yields values of  $\delta$  accurate to  $\pm 1$  nm in the range 2-20 nm, given that  $\delta$  is smaller than  $\kappa^{-1}$ .

In addition to  $\delta$ , the layer thickness as a function of time or the kinetics of polymer adsorption may be obtained. The ability to analyze the kinetics of the polymer adsorption and desorption is information that cannot be obtained from dynamic light scattering experiments, the traditional method for measuring  $\delta$  on colloidal particles.<sup>13</sup> The rate of adsorption of polymers is driven by two processes 1) transport of the polymer to the surface by convection and/or diffusion and 2) attachment of the polymer to the interface. The second process may involve rearrangement of the chains towards more desirable states as well as possible entanglements between chains. Dijt et al. have shown that the adsorption process for poly(ethylene oxide), PEO, on SiO<sub>2</sub> from a well-defined flow is mass transfer limited until near saturation. That is step 1) is the rate limiting step until 70 – 100% of the adsorption plateau value is achieved. Their results are in good agreement with ATR-IR results of Van der Beek et al. for poly(tetrahydrofuran), results by Johnson and Granick for poly(methyl methacrylate), and studies by Frantz et al. for polystyrene.<sup>9</sup>

#### 4.3. Materials

The physical characteristics and source of the PEO and poly(2-ethyl-2-oxazoline), PEOX, homopolymers used in this study are listed in Table 4.3.1. NaCl was purchased from Fischer Scientific for making 1 x  $10^{-3}$  M reagent grade buffer solutions. The water used for preparing all solutions in these studies was filtered through a Barnstead NANOpure II water purification system, and had a specific resistance of greater than 17 MΩ-cm.

Table 4.3.1. Physical properties of the polymers used in streaming potential experiments.

Polymer	Source	Batch #	$M_w \ g\!/mol$	Ν	PI
PEO	Pressure Chemicals	344-EO	334.5K	7600	1.14
	Polymer Laboratories	20835-7	120K	2730	1.02
	Polymer Laboratories	20839-6	460K	10,460	1.06
PEOX	Oxazogen, Inc.	467-16	10K	100	1.1-1.15
	Oxazogen, Inc.	497-79	30K	300	1.1-1.15
	Polymer Chemical Innovations	941115	29.4	300	2.2

#### 4.4. Experimental Setup

Figure 4.4.1 is a schematic of the streaming potential instrument. A fused silica capillary was mounted between an inlet and outlet electrode. The capillary was a standard type used for chromatography, and had an outer coating of polyimide to allow it to be bent without cracking. It was purchased from Alltech Associates, Inc. The electrodes were Ag/AgCl, and were positioned in the top of a Teflon T-section. The were made from 0.5 mm 99.9985% Puratronic® silver wire. Chloride was deposited by immersion in 0.1N HCl, while hooked up as a positive electrode with platinum wire as the negative electrode. Current was passed at 0.4mA/cm<sup>2</sup>, with the silver wire immersed in the 0.1N HCl solution for approximately 1.5 minutes.

The electrodes were connected to an Orion SA 720 pH meter, which was capable of measuring voltage changes to  $\pm 0.01$  mV. By insertion into the T-section, the electrodes were placed directly in the flow path. To accommodate the small capillary, the smallest standard O-rings supplied with the T-sections were replaced with 0.5mm inner diameter peristaltic pump tubing from Fisher Scientific. The capillary was inserted in the tubing such that 1-2 mm were exposed at each end. The largest O-rings supplied with the T-sections were fit on the peristaltic pump tubing, and the assembly was attached to the T-sections. The peristaltic pump tubing served both as an O-ring to seal the capillary assembly and as shield from electromagnetic radiation, i.e. a Faraday cage. A manual, three-way, Teflon inlet valve was positioned upstream of the electrodes, and was connected to two tanks, one containing buffer solution and the other the polymer solution, via 1/16in. silicone surgical grade tubing. Omnifit manufactured all the Teflon fittings.

Each tank sat on a jack so that its height could be adjusted to maintain a near constant and equal hydrostatic head. In addition, the two tanks were connected to a nitrogen cylinder. The nitrogen was used to provide overpressure, which allowed a constant flowrate of solution through the system to be maintained. An overpressure of approximately 19 - 20 kPa was used. The tanks were sized so that the system would run for over 300 seconds with less that 1% change in hydrostatic head. The buffer and polymer tanks were 1 liter



Figure 4.4.1. Schematic of Streaming Potential Instrument.

Nalgene <sup>®</sup> LDPE bottles with tubing connect caps that allowed nitrogen to enter at the top and the fluid to exit at the bottom. The buffer tank maybe was as large as a 2.5 gallon Nalgene <sup>®</sup> LDPE carboy with spigot. Large quantities of buffer are made in the 2.5 gallon Nalgene <sup>®</sup> LDPE carboy with spigot for use in all polymer solutions to prevent error due to variations in buffer concentration. 1 x 10<sup>-3</sup> M NaCl was used, giving a value of  $\kappa^{-1} =$ 9.6 nm.

The capillary/electrode system was housed inside a Faraday cage made from a standard 9"x13" aluminum cake pan which was covered by a 15" aluminum cookie sheet. This was necessary to shield the system from background electromagnetic interference, such as fluorescent light and laboratory instruments. The sheet and pan could be bolted together to insure contact, though this was proven to be unnecessary. The capillary was bent into a U-shaped configuration for additional noise reduction. Plastic stand pieces designed to hold graduated cylinders were adhered to the bottom of the cake pan. Cut to fit the Teflon T-sections, they were used to hold them in position. The three-way valve was adhered to the top of the Faraday cage and all tubing and electrode wires entered the cage through holes drilled in the cookie sheet. The Faraday cage was mounted on rubber feet made of 2 #6 stoppers taped together and velcroed to the bottom of the cage. The entire assembly was then placed inside a metal file cabinet. The cabinet had a lid which could be closed to provide additional shielding, if necessary, and was on wheels making the system mobile. The cabinet was grounded to the nitrogen line, which in turn was grounded to a wall outlet.

Expended solution exited the Faraday cage and was delivered to a 2.5 gallon plastic gas can that was located on a shelf below the file storage compartment. The shelf area was shielded with wire screen of sufficiently small mesh to block electromagnetic radiation. As an extra precaution, the exit stream, made of surgical grade silicone tubing, was wrapped in a metal braid for further shielding. A door was constructed to allow the gas can to be removed and emptied. The flowrate was conveniently checked by measuring the weight of exiting solution as a function of time for a given overpressure, or by attaching the exit stream to a Cole-Parmer Model 65 mm aluminum/SS flowmeter. Typical experimental

parameters were a mass flowrate of 2.148 - 2.214 g/min or  $\pm$  1.5% of the optimum flowrate of 2.181g/min. These mass flowrates were equivalent to volumetric flowrates of 2.148-2.214 cm<sup>3</sup>/min. At 2.181 cm<sup>3</sup>/min the shear rate at the wall was 11,300/sec, the typical value employed by Dijt et al.<sup>9</sup> in similar experiments. These corresponded to a Reynolds number range of 142.4 - 146.8, and therefore well within the laminar flow regime. The capillary was sufficiently long to insure negligible end effects.

The silica capillaries were cleaned via a continuous flow procedure. A 20 cc glass syringe of Chromerge (0, a) sulfuric acid/potassium permanganate cleaning solution sold by Fisher Scientific, was attached by 1/16" ID Teflon tubing to an Omnifit Teflon 2-way fitting. The capillary was mounted in the fitting opposite the Teflon tubing. The syringe was clamped to a ringstand so that gravity would force the chromerge to flow through the capillary. By setting weights on the syringe plunger, the flow through the capillary was adjusted to allow continuous cleaning from 4-24 hours. A minimum of 4 hours was used, but usually 8 hours was allowed. Similarly, a 20 cc glass syringe of 2M nitric acid was setup to follow the chromerge wash, and it too utilized gravity flow to pass through the capillary for a minimum of 4 to 8 hours. After cleaning with acid, the capillaries were flushed with 10 cc or more of deionized water or 1 x 10<sup>-3</sup> M NaCl solution. The capillaries were then used immediately or stored containing 1 x 10<sup>-3</sup> M NaCl, and sealed at each end with 1/4" silicone rubber septum from Alltech Associates, Inc. The capillaries were usually used in 1-3 days, so no storage lifetime was determined.

#### 4.5. Results and Discussion

#### 4.5.1. Instrument Calibration

Before any polymers were evaluated for their adsorption properties, the instrument was calibrated. The calibration was completed in several stages. First, the flow rate control from each tank was established. The ability to get equivalent flowrates from each tank at a given nitrogen pressure and fluid height was essential. Once flowrates were equivalent, it was necessary to verify that for the same solution, equivalent millivolt readings were obtained for consecutive openings and closings of the three-way valve. This would insure that air bubbles were not trapped within the system, that desorption experiments could be

performed, and that the potentials measured for the buffer and polymer solutions could be used to calculate the layer thickness,  $\delta$ . Finally, experiments with a polymer of known molecular weight and whose hydrodynamic layer thickness was established at various concentrations was necessary to demonstrate the accuracy of the measurements of  $\delta$ . As stated above, several well-characterized samples of PEO were used for calibration purposes.

For the same nitrogen pressure and equal hydrostatic head, flowrates of buffer and polymer solutions were observed to be different by less than 1% or 0.02 g/min. At these conditions, the millivolt readings for buffer solutions were within 0.5% or 1 mV of each other. The typical noise level for flow from one tank was  $\pm 1$  mV. Typical results are shown in Table 4.5.1. Based on this demonstration of sufficient flow rate control and suitable reproducibility of streaming potential with buffer solutions, polymer calibration runs with the PEO were completed.

Figure 4.5.1 shows the calibration curve for PEO with  $M_w = 334.5$ K g/mol, 460K g/mol and 120K g/mol versus data from Dijt and coworkers for PEO.<sup>9</sup> The error bars depicted are representative of the typical error for all streaming potential data. They are were calculated as

$$\sigma_{\delta} = \kappa^{-1} \cdot \left[ \left( \frac{1}{V_{\delta}^{O}} \right)^{2} + \left( \frac{1}{V_{\delta}^{P}} \right)^{2} \right]^{\frac{1}{2}}$$
[4.5.1]

where  $V_s^{0}$  and were the potentials measured due to the flow of the buffer solution and polymer solutions, respectively.  $\kappa^{-1}$  was the debye length, equal to 9.6 nm for a 1 x 10<sup>-3</sup> M NaCl buffer solution. The derivation of equation [4.5.1] is given in Appendix D, and error bars shown in all remaining figures were calculated similarly. Table 4.5.1. Calibration Data to Verify Equal Properties of the Buffer and Polymer Tanks

	N <sub>2</sub> Pressure	<b>Buffer Tank</b>	Polymer Tank	<b>∆%</b> *
Run #1 Flowrate, g/min ∆V, mV	44 kPa	4.325	4.332	0.16 -
Run#2 Flowrate, g/min ∆V, mV	19.5 kPa	2.18	2.19	0.46
Run#3 Flowrate, g/min ∆V, mV	20 kPa	2.184 145.5	2.204 145	0.92 0.03
Run#4 Flowrate, g/min ∆V, mV	20 kPa	2.15 139.5	- 139.5	- 0.00

\*  $\Delta\% = [(Buffer Tank - Polymer Tank)/Buffer Tank]*100\%$ 



Figure 4.5.1. Streaming potential determination of the hydrodynamic layer thickness,  $\delta$ , versus concentration for several well defined samples of PEO.  $\blacksquare$  represent PEO data of Dijt. et al. (ref. 7).

Based on the above data, the instrument was considered to be accurate and thus capable of measuring the hydrodynamic layer thickness accurately for the desired PEOX samples. While the hydrodynamic layer thicknesses were comparable, some differences existed between our instrument and that of Dijt. Dijt reported the baseline potentials for the buffer as 155-160 mV. Typically, baseline voltages of 106-110 mV were observed in our

experiments. This difference in the absolute value of the baseline potential probably resulted from Dijt's use of a glass capillary versus the author's use of a fused silica capillary. Given the similarity in the data, this did not appear to promote an error in the data. Dijt et al. reported hydrodynamic layer thicknesses for samples at  $1 \times 10^{-7}$ g PEO/g solution and  $1 \times 10^{-8}$ g PEO/g solution that were extremely low and difficult to reproduce. As seen in Figure 4.5.1, data were not obtained below a concentration of  $1 \times 10^{-6}$ g PEO/g solution on this instrument. While it would have been desirable to have the increased sensitivity, it was not essential, and good agreement between the instruments was achieved in the range over which data was obtained. Finally, the initial lagtime in this system was 5-8 seconds longer than that observed by Dijt et al. for their instrument. The delay results from deadspace introduced when switching the three-way valve from one solution tank to the other. This delay was only important to the measurement of adsorption and desorption kinetics, as the initial slope would be obscured. Final equilibrium layer thickness values were not affected.

#### 4.5.2. PEOX Homopolymer Results

Once calibrated, the PEOX samples were run at concentrations of 1 x 10<sup>-6</sup> g PEOX/g solution up to 1 x 10<sup>-4</sup> g PEOX/g solution. The data for the PEOX  $M_w = 10K$  g/mol,  $N_{PEOX} = 100$  at 1 x 10<sup>-4</sup> g PEOX/g solution were similar to literature values for PEO at  $M_w = 7K$  g/mol,  $N_{PEO} = 110$ , and PI = 1.02, as shown in Figures 4.5.2 and 4.5.3. Similar agreement was observed for the PEOX 30K g/mol,  $N_{PEOX} = 300$  versus PEO with  $M_w = 23K$  g/mol,  $N_{PEO} = 520$ , also shown in Figures 4.5.2 and 4.5.3. The thickness  $\delta$  increased with increasing concentration, as illustrated in Figure 4.5.3 where  $\delta$  is plotted versus the adsorbed amount,  $\Gamma$ . This trend was expected due to the increase in chain-chain interactions as higher levels of polymer adsorb. The chain-chain interactions led to the

formation of more loops and tails, which corresponds to an increase in the adsorbed layer thickness,  $\delta$ . An unexpected trend was observed, however, as the value of  $\delta$  for N<sub>PEOX</sub> = 300 was greater than that for N<sub>PEO</sub> = 520. While the trend was not expected, it was considered reasonable given the complex dependence of  $\delta$  on the segmental interaction parameter,  $\chi_s$ ,  $\chi$  the Flory-Huggins solution parameter, N, and excluded volume parameters, as discussed in Chapter 2.

Comparing the measured adsorbed layer thickness to the polymer end-to-end distance, h, provides a significant insight into the difference in the conformation of the polymer chains on a surface versus that for the free polymer chains in solution. The parameter h is defined as<sup>10</sup>

$$h = \left(\frac{L_{\kappa} l_0 M}{m_0}\right)^{\sqrt{0.5}}$$
[4.6.1]

where  $L_K$  is the Kuhn length,  $l_0$  is the length per bond of a monomer unit, M is the monomer molecular weight, and  $m_0$  is the molecular weight per bond of a monomer. h is related to the radius of gyration as  $R_g = h \cdot 6^{-0.5}$ . Using the parameters determined by Chen et al.<sup>11</sup> for PEOX homopolymer, for PEOX  $M_w = 30K$ , h = 9.1 nm. For PEOX  $M_w = 10K$ , h = 5.3 nm. In both cases, the adsorbed layer thickness was observed to be significantly smaller, indicating the conformation of the PEOX chains on the SiO<sub>2</sub> surface was significantly different from that of the polymer chain free in solution.

In general, the data illustrate typical adsorption behavior of strongly adsorbing homopolymers which tend to adsorb in flat train configurations at low values of  $\Gamma$ , and only begin to adopt the more extended configurations of loops and in particular, tails, at higher values of  $\Gamma$ . It is significant that the highest value of  $\delta$  measured for the PEOX  $M_w$ = 30K homopolymer was about 4.4 nm. This value was significantly less than  $\delta$  for extended brush layers formed by block copolymers. Killman et al.<sup>12</sup> have measured  $\delta$ =10-15 nm for PEO-PPO-PEO, PPO stands for poly(propylene oxide), triblock copolymers



Figure 4.5.2. Determination of the adsorbed layer thickness,  $\delta$ , versus concentration for several PEOX homopolymers compared to PEO data of Dijt et al. (ref 7).  $\blacksquare$  represent PEO data of Dijt et al.



Figure 4.5.3. Plot of streaming potential layer thickness,  $\delta$ , versus the adsorbed amount,  $\Gamma$  for PEOX homopolymers compared to PEO data of Dijt et al. (ref. 7). The values of  $\Gamma$  for PEOX are estimated from the data of Chen et al. (ref 12).  $\blacksquare$  represent data for PEOX homopolymers.  $\bigcirc$  represent PEO data of Dijt. et al.

adsorbed onto spherical polymer latex particles.

In addition to  $\delta$ , the kinetics of adsorption were determined. Figure 4.5.4 shows the kinetics for the experiments where PEOX  $M_w = 29.4$ K concentration was varied. Equilibrium was reached after 500 seconds for the 1 x 10<sup>-6</sup> g PEOX/g solution, whereas for a concentration of 1 x 10<sup>-4</sup> g PEOX/g solution, equilibrium was attained at 400 seconds. This trend of longer time for equilibrium at the lower concentration was expected since as the concentration of PEOX was increased, the driving force for adsorption was increased. The thickness,  $\delta$ , increased with increasing concentration since more polymer adsorbed on the SiO<sub>2</sub> surface. The observed timescale needed to reach equilibrium was similar to that observed by Dijt et al., who showed that the kinetics of adsorption in this case was controlled by the diffusion of the polymer chains from the solution to the capillary wall.

In theory, the desorption of the homopolymers could be studied. Given the timescale for desorption, as discussed by Dijt et al.<sup>9</sup> and Fleer et al.<sup>14</sup>, it was not practical. After adsorption of PEO  $M_w = 330$ K onto a silica capillary at 1 x 10<sup>-6</sup> g PEOX/g solution, the buffer solution was allowed to flow back into the capillary. An initial decrease of approximately 22% in the layer thickness was observed in the first 1-2 minutes of flow. After 1-2 minutes, the layer thickness stayed level over a period of 4 minutes after which time the buffer flow was stopped, and the polymer flow was started. The original layer thickness of 8.6 nm was recovered. Repeated flow of buffer solution lead to a 12% decrease in layer thickness, with apparent steady state reached again in 1-2 minutes. No change in the layer thickness was observed during the timeframe from 2 –7 minutes.

# 4.6. Conclusions/Future Work

A streaming potential instrument was built which was capable of measuring the layer thickness of nonionic polymers adsorbed on a fused  $SiO_2$  capillary. Layer thickness values for PEOX homopolymer were measured with values of approximately 1nm and 4.4 nm for



Figure 4.5.4. Streaming potential determination of the adsorbed layer thickness,  $\delta$ , versus time as a function of polymer concentration for PEOX  $M_w = 29.4$ K homopolymer.

PEOX  $M_w = 10K$  and  $M_w = 30K$ , respectively. An unexpected trend was observed in which the layer thickness for an  $N_{PEOX} = 300$  was greater than that for  $N_{PEO} = 520$ . While the trend was not expected, no definite explanation of the phenomena could be offered based on streaming potential and adsorption isotherm results, from Chapter 3, alone. The development of this instrument was fundamental to establishing a technique for determining the layer thickness of nonionic diblock copolymers, which will be designed as steric stabilizers for submicron metal oxide particles in aqueous media.

From competitive adsorption experiments with well-defined PEOX and PEO homopolymers, Chen et al. determined that PEOX adsorbs preferentially on SiO<sub>2</sub> over PEO for samples of PEO and PEOX with similar values of N<sub>PEOX</sub> and N<sub>PEO</sub>. For N<sub>PEO</sub>  $\geq$  10N<sub>PEOX</sub>, PEO displaced PEOX from the SiO<sub>2</sub> surface.<sup>11</sup> Given this and the high adsorption behavior observed in the adsorption isotherm experiments described in Chapter 3 and those of Chen et al., for future work, diblock copolymers of PEOX-PEO should be synthesized for streaming potential adsorbed layer thickness measurements. In such a system, PEOX would be designed to be the anchor block and PEO the tail block.

The measured layer thicknesses for the diblock copolymers are expected to scale according to  $\delta \propto \frac{N_{tail}}{N_{anchor}}$ , as predicted by the scaling theory of Marques and Joanny, and verified by Guzonas et al.<sup>10</sup> Guzonas et al. observed tail extensions greater than twice the end-to-end distance of polystyrene, PS, for PS-PEO diblock copolymers adsorbing on mica from toluene, where PEO was the anchor block. The adsorbed amounts of the anchor block,  $\Gamma_{PEO}$ , were relatively low, being in the range of 0.1 mg/m<sup>2</sup>. Based on the results of Guzonas et al. and the work of Chen et al., it is anticipated that PEOX-PEO diblock copolymers should be capable of forming a brush structure on SiO<sub>2</sub>.

Currently, only adsorbed layer thicknesses on  $SiO_2$  is feasible on the streaming potential instrument due to the avilability of appropriate capillaries. However, a flat plate method has been designed, which bears investigation.<sup>15</sup> The ability to use flat plates would

potentially widen the capability of the instrument, as substrates such as  $Al_2O_3$  would be available. High purity  $Al_2O_3$  is a common substrate in semiconductor manufacturing. In theory, flat plates on any material could be cast or molded, as the first use of the flat plate design was the zeta potential measurement of polymer films.

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