Macromolecules 1988, 21, 1016-1020

Effect of Applied Potential on the Ellipsometric Thickness of Sodium Poly(styrenesulfonates) Adsorbed on a Platinum Surface

Masami Kawaguchi,* Kasumi Hayashi, and Akira Takahashi

Department of Industrial Chemistry, Faculty of Engineering, Mie University, 1515 Kamihama-cho, Tsu, Mie 514, Japan. *Received April 24, 1987*

ABSTRACT: The thickness of a sodium poly(styrenesulfonate) (NaPSS) layer adsorbed on a platinum plate was measured by ellipsometry in aqueous NaCl solutions as a function of molecular weight, solvency, and applied potential. The applied potentials correspond to cathodic and anodic potential differences relative to the rest potential. At the negative potential differences, with an increase in potential difference the thickness of the adsorbed layer increases and its variation with the molecular weight decreases. The exponent of the molecular weight dependence of the thickness almost becomes zero at the large negative potential differences. Thus, small NaPSS chains are subjected to larger deformation with potential difference than large ones. On the other hand, at positive potential differences, the adsorbed layer thickness of small NaPSS chains shows little change, but that of large ones is much squeezed with increasing potential difference.

Behavior of polyelectrolyte adsorption on solid surfaces from its solution should strongly depend on the polyelectrolyte charges as well as charges of the surfaces. For example, negatively charged polyions tightly adsorb on oppositely charged surfaces by adopting a relatively flattened conformation due to the electrostatic attraction between polyion and surface. It will be expected that, in contrast, that the polyion chains would take an extended conformation if they were adsorbed on the same charged surfaces. Such speculations are in agreement with some theories[1-4] on polyelectrolyte adsorption, which are treated as an extension of a mean-field theory for the adsorption of nonionic polymers.

The thickness of the adsorbed polyelectrolyte layer, which may give insight into the conformation of adsorbed polyelectrolyte chains, has been obtained by various techniques such as flow through porous media,[5,6] ellipsometry,[7-9] surface force measurement,[10] and photon correlation spectroscopy.[11] These techniques generally give a mean value of the thickness that depends on the technique used. Variation of the thickness of the adsorbed polyelectrolyte layer measured by these different methods with molecular weight as well as salt concentration gives a qualitative agreement. However, most data have been concerned with the adsorption of polyelectrolyte on the uncharged surface.

Recently, Cosgrove, Obey, and Vincent[11] have measured the hydrodynamic thickness of sodium poly(styrenesulfonate) (NaPSS) on polystyrene latex particles with negatively or positively charged surface by using photon correlation spectroscopy. The hydrodynamic thicknesses of NaPSS adsorbed on latex particles with high positive or negative surface charges are remarkably similar, but for very low positive surface charges NaPSS chains take a more extended conformation.

Ellipsometry is able to in situ determine polyelectrolyte layer thickness adsorbed on a platinum plate as a function of imposed potential since potentials can be applied to the platinum plate. In this paper we study the adsorption of an anionic and strong polyelectrolyte, NaPSS having a relatively narrow molecular weight distribution, on a platinum plate with applied potential in aqueous NaCl solutions as a function of molecular weight. Variation of NaPSS adsorbed layer thickness with applied potentials, which are anodic and cathodic relative to the rest potential, will be discussed in terms of the conformation changes of adsorbed linear polyelectrolyte chains.

Experimental Section

Materials. Four NaPSS prepared by sulfonation of polystyrene with narrow molecular weight distributions were purchased from Pressure Chemical Co. Characteristics of NaPSS given by the manufacturer are listed in Table I.

Water was doubly distilled in an all-Pyrex apparatus. Analytical grade NaCl was used without further purification.

A platinum plate (12 × 57 × 0.5 mm) was used as an adsorbent. It was cleaned by soaking in a hot concentrated aqueous HNO_3–H_2SO_4 (1:1 volume) solution and washed fully with the distilled water. This treatment has been used in previous studies.[8,9]

Ellipsometry. Adsorption measurements of NaPSS onto a platinum plate were performed at 25 °C by using a Shimadzu P-10 ellipsometer.[8,9] The cleaned platinum plate was assembled vertically in a glass cell filled with 200 mL of aqueous NaCl solution.

The glass cell was constructed especially for in situ ellipsometric studies at controlled potential as shown in Figure 1. The working electrode corresponding to the platinum plate is electrically in contact with a silver plate. The counter electrode was made from a platinum plate (20 × 10 × 0.1 mm), which is placed in a glass tube attached the bottom with a glass filter. A Ag/AgCl reference electrode, maintained in a separate compartment, is connected to the cell by an agar bridge equipped with a Luggin Capillary and is placed close to the working electrode. These electrodes are connected with a Hokuto Denko HA 303 potentiostat.

The light source was a Toshiba SHL-100 UV high-pressure mercury lamp. The wavelength of the incident light was 546 nm, and the incident angle was 70°. The average refractive index, n_f, and the thickness, t, of the adsorbed layer were calculated from a FACOM 230 computer from the experimental values of the phase difference Δ and the azimuth angle ψ of the amplitude ratio with an iterative procedure, in which the refractive index and thickness are sought which reproduce the experimental values of Δ and ψ. In computer calculation, we assume the adsorbed NaPSS layer to be homogeneous.

The measured bulk concentration (0.04 g/100 mL) was well in the plateau regions of adsorption isotherms of NaPSS for both the thickness and adsorbed amount, independent of molecular weight as well as added NaCl concentration.[8,9] Aqueous 0.1 M and 4.17 M NaCl solutions at 25 °C are good and Θ-solvent conditions for NaPSS, respectively.[12]

Results and Discussion

Effect of Applied Potential on a Clean Platinum Plate. First, we have paid attention to the effect of potential differences between applied and rest potentials, ranging from 250 to 450 mV, on the refractive index of a clean platinum plate immersed in aqueous 0.1 or 4.17 M NaCl solution before adsorption of NaPSS. The experimental differences in Δ and ψ between at rest and applied potentials did not exceed the experimental errors of $\pm 0.01°$ for Δ and $\pm 0.005°$ for ψ both in aqueous NaCl solutions, respectively. Therefore, applied potentials give no change in the refractive index of a clean platinum plate.

Effect of Applied Potential on the Adsorbed Amount of NaPSS. When NaPSS molecules are adsorbed on a platinum plate the change in refractive index of the solution near the platinum surface leads to changes

0024-9297/88/2221-1016$01.50/0

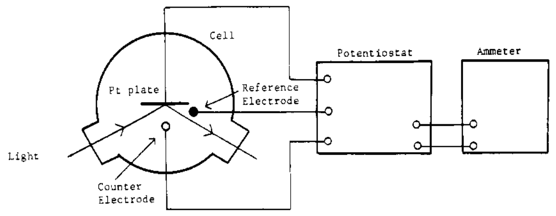

Figure 1. Schematic diagram of ellipsometry cell apparatus for applied potential measurements.

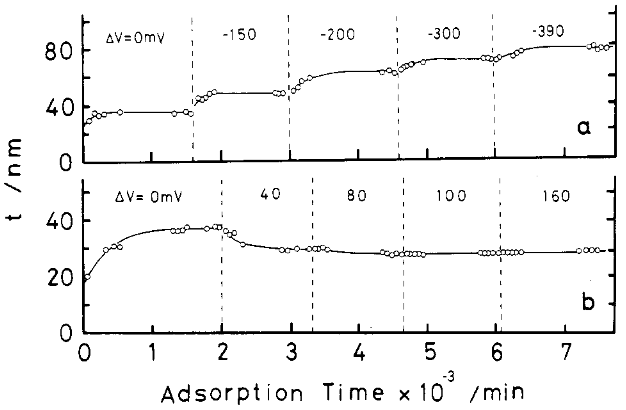

Figure 2. Adsorbed layer thickness t versus adsorption time for NaPSS-4 in aqueous 4.17 M NaCl solution: (a) negative potential differences; (b) positive potential differences. The number between the dashed vertical lines indicates the potential difference between applied and rest potentials.

in Δ and ψ. The quantities $\delta\Delta$ and $\delta\psi$, being differences between values after and before and adsorption, are larger than −1.5° and smaller than 0.4°, respectively.

The ellipsometric adsorbed amount of polymer usually is obtained from the t and n_f values by assuming that the n_f is a linear function of polymer concentration in the adsorbed polymer layer.[13] However, such a relation cannot be applied to adsorption of polyelectrolyte in added salt solutions because the adsorbed layer and bulk phase are considered to be a three-component system, which consists of polyion, small ion, and water. Thus, in previous papers[7-9] we have proposed a method to evaluate the adsorbed amounts of polyelectrolyte and salt by assuming that n_f is represented by the Lorentz–Lorenz equation, and the Donnan equilibrium is held between the bulk phase and the adsorbed layer. Strictly speaking, this method cannot be applied to calculate the adsorbed amount of polyelectrolyte at impressed potentials because the effect of surface charge density is not taken into account. Since it is important to know the amount of adsorbed polyelectrolyte under potential variation, we try to calculate the amount adsorbed by the method described previously.[7-9] It was found that the amount of adsorbed NaPSS shows a slight decrease with increasing negative potential difference and an increase with increasing positive potential difference. Moreover, we confirmed that t and n_f values at zero applied potential do not change before and after applied potentials. These results seem to indicate that the amount of NaPSS is almost constant under potential variation.

Adsorption Kinetics under an Applied Potential. Figure 2 shows typical plots of the thickness of adsorbed NaPSS-4 in aqueous 4.17 M NaCl solutions at stepwise changes in applied potential as a function of adsorption time. The numbers in Figure 2 indicate the potential difference ΔV.

The rest potential generally depends on the property of the adsorbing polymers[14] as well as bulk phase condition[15] but in this study it occurred at 550 ± 30 mV independent of molecular weight of adsorbing NaPSS and NaCl concentration. (The rest potential of the clean platinum plate usually occurred at around 450 ± 10 mV in aqueous 0.1 and 4.17 M NaCl solutions.) At negative ΔV the thickness of the adsorbed layer rapidly increases at the beginning stage of changes in the applied potential and shows a gradual increase with adsorption time and then reaches a plateau value within 10^3 min.

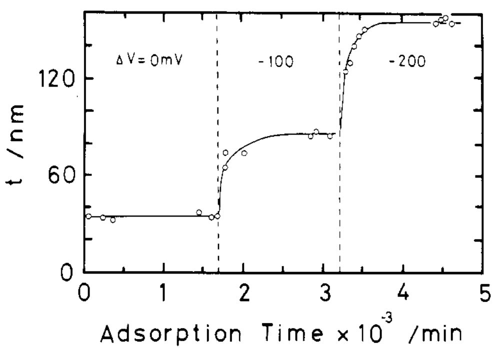

Figure 3. Adsorbed layer thickness t versus adsorption time for NaPSS-2 in aqueous 0.1 M NaCl solution at negative potential differences. The number between the dashed vertical lines indicates the potential difference between applied and rest potentials.

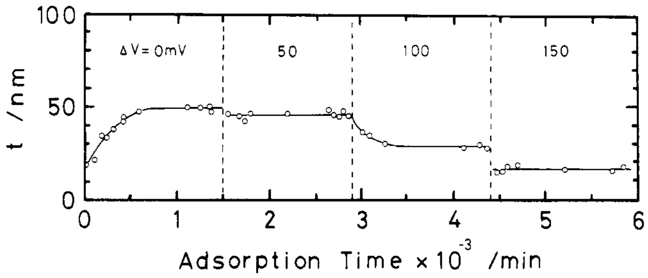

Figure 4. Adsorbed layer thickness t versus adsorption time for NaPSS-3 in aqueous 0.1 M NaCl solution at positive potential differences. The number between the dashed vertical lines indicates the potential difference between applied and rest potentials.

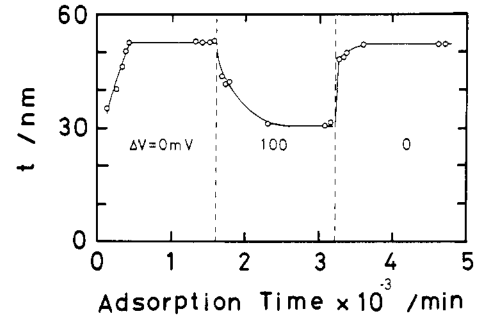

Figure 5. Adsorbed layer thickness t versus adsorption time for NaPSS-3 in aqueous 0.1 M NaCl solution by cyclic changing potential differences; i.e. $\Delta V = 0 \rightarrow 100 \rightarrow 0$ mV.

With an increase of negative ΔV the thickness of the adsorbed layer increases to larger values than that obtained at the rest potential. As a result the average refractive index in the adsorbed NaPSS layer becomes smaller.

Figure 3 shows the thickness of the adsorbed layer for NaPSS-2 in aqueous 0.1 M NaCl solution at the negative ΔV as a function of adsorption time. Variation of the thickness with ΔV behaves similarly to the large molecular weight sample. On the other hand, at positive ΔV the thickness of the adsorbed layer drops at the beginning stage and attains a constant value as seen from Figures 2b and 4. Figure 4 displays the thickness of the adsorbed

Table I
Characteristics and Adsorption Data of Poly(styrenesulfonates)

sample	$M_w \times 10^{-3}$, g mol^{-1}	NaCl, M	$2\langle S^2\rangle^{1/2}$, nm	ΔV, mV	t, nm	n_f
NaPSS-1	88	4.17	$10._4$	100	12	1.395_4
				0	12	1.395_4
				−100	28	1.380_4
				−200	45	1.377_2
				−300	52	1.376_2
				−390	85	1.375_4
		0.1	$23._9$	100	28	1.340_1
				0	28	1.340_1
				−50	39	1.338_6
NaPSS-2	117	4.17	$15._3$	100	12	1.391_6
				50	14	1.391_6
				0	17	1.390_6
				−100	33	1.380_4
				−200	64	1.376_7
				−300	86	1.376_0
				−390	100	1.375_8
		0.1	$39._6$	100	31	1.344_0
				50	31	1.344_0
				0	35	1.342_1
				−100	95	1.337_2
				−200	156	1.336_9
NaPSS-3	354	4.17	$20._4$	150	17	1.391_6
				100	17	1.391_6
				50	24	1.379_0
				0	24	1.379_0
				−50	31	1.378_1
				−100	52	1.377_9
				−200	67	1.376_9
				−300	77	1.376_5
				−390	87	1.376_4
		0.1	$60._4$	150	16	1.342_1
				100	30	1.340_1
				50	46	1.377_6
				0	52	1.337_6
				−50	75	1.337_4
				−100	128	1.337_0
				−200	152	1.336_9
				−300	161	1.336_9
NaPSS-4	1060	4.17	$39._8$	160	29	1.386_0
				100	29	1.386_0
				80	29	1.386_0
				40	30	1.386_0
				0	37	1.381_8
				−100	37	1.381_8
				−200	65	1.378_8
				−300	73	1.378_5
				−390	79	1.378_1
		0.1	11_7	140	31	1.340_1
				100	33	1.339_5
				80	42	1.338_6
				40	55	1.337_6
				0	80	1.337_1
				−100	80	1.337_1
				−200	128	1.337_0
				−300	158	1.336_9
				−390	168	1.336_9

layer for NaPSS-3 in aqueous 0.1 M NaCl solution at positive ΔV as a function of adsorption time.

Figure 5 shows a typical plot of the adsorbed layer thickness against adsorption time when ΔV is reduced to zero from a given potential difference: the thickness almost returns to the earlier value at the rest potential. However, the thickness of the adsorbed layer at the zero potential when approached from the highest negative potential difference ΔV = −390 mV is somewhat larger than the earlier thickness at the rest potential. Thus, at the higher negative potential differences the data of the thickness seems not to be the equilibrium data. This indicates that more experiments are necessary to confirm the reversability of the adsorbed layer thickness under impressed potentials.

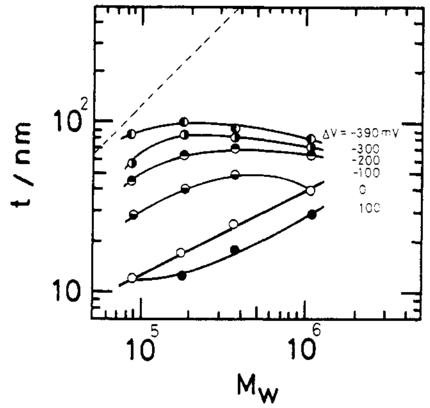

Figure 6. Double-logarithmic plot of adsorbed layer thickness versus molecular weight of NaPSS in aqueous 4.17 M NaCl solution. The number indicates the potential difference between applied and rest potentials. Dashed line indicates the contour length of a free NaPSS chain.

For the lower molecular weight samples of NaPSS-1 and NaPSS-2 in aqueous 0.1 M NaCl solution, the adsorbed layer thicknesses at potentials more negative than ΔV = −200 mV for NaPSS-2 and ΔV = −100 mV for NaPSS-1 are so scattered that data are not reported here.

Replicate measurements showed that the errors of t in aqueous 4.17 and 0.1 M NaCl solutions are less than 3% and 10% even under potential variation, respectively, and the reproducibility in n_f is good. In Table I, data of t and n_f at the plateau state for adsorption time are summarized. In the same solvent all n_f values are larger than the refractive index of the solvent, i.e., 1.3720 for aqueous 4.17 M NaCl solution and 1.3352 for aqueous 0.1 M NaCl solution.

Small current densities of approximately 2.3 μA/cm^2 at ΔV = −100 mV, 9.6 μA/cm^2 at ΔV = −200 mV, 22 μA/cm^2 at ΔV = −300 mV, 33 μA/cm^2 at ΔV = −400 mV, and 0.6 μA/cm^2 at ΔV = 100 mV were typically obtained when these potentials are first imposed. Thus, the platinum plates with more negative and positive potentials relative to the rest potential behave as more negatively and positively charged surfaces than those at the rest potential, respectively. However, we cannot estimate the actual surface charge density. Intuitively, we expect that (1) for a polyelectrolyte chain adsorbed on the same charged surface the thickness of the adsorbed layer would increase with an increase of the negative charge on the surface due to the electrostatic repulsion and (2) for a polyelectrolyte chain adsorbed on the opposite-sign charged surface the adsorbed layer would become a more dense and thinner layer with increasing surface charges owing to electrostatic attractive force. Thus, adsorbed NaPSS chains behaved as expected (see Table I). Since the real surface charge density is unknown in this study we will discuss the conformation change of adsorbed NaPSS chains as a function of ΔV.

Plateau Thickness in Aqueous 4.17 M NaCl Solution. Figure 6 shows plateau values of the adsorbed layer thickness plotted double logarithmically against the molecular weight in aqueous 4.17 M NaCl solution. At the rest potential the thickness of the adsorbed layer is proportional to the square root of NaPSS molecular weight and almost equals the diameter of a NaPSS chain in bulk solution as shown in Table I. The radii of gyration $\langle S^2\rangle^{1/2}$ given in Table I are estimated from the radius of gyration–molecular weight relations obtained by Takahashi, Kato, and Nagasawa.[12] Therefore, under Θ-solvent conditions at the rest potential, the molecular weight dependence of the adsorbed layer thickness for NaPSS is in fact

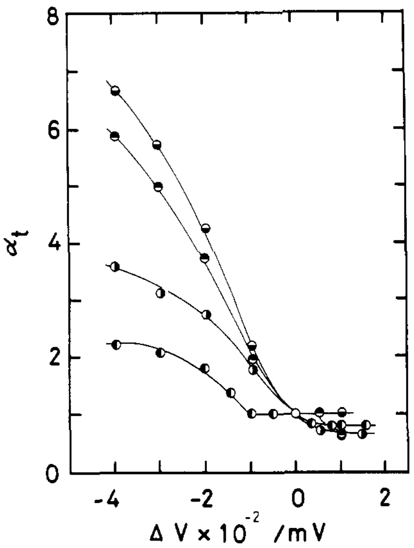

Figure 7. Expansion factor α_t defined as the ratio of thickness at applied potential to that at rest potential in aqueous 4.17 M NaCl solution as a function of potential difference: (◒) NaPSS-1; (◓) NaPSS-2; (◑) NaPSS-3; (◐) NaPSS-4.

quite similar to that for adsorption of nonionic polymers.[16-20]

The thickness of the adsorbed layer at the applied potential in aqueous 4.17 M NaCl solution, however, shows a markedly different behavior. At constant molecular weight the thickness of the adsorbed layer increases with increasing negative ΔV, while the thickness at positive ΔV is lower than that at the rest potential. Molecular weight dependence of the thickness of adsorbed layer at negative ΔV becomes weaker with increasing ΔV. In particular, at $\Delta V = -390$ mV the thickness of the adsorbed layer is almost constant irrespective of molecular weight, and, moreover, its absolute value for the lowest molecular weight sample is comparable to the contour length of NaPSS chain, which is represented by a dashed line in Figure 6. Thus small adsorbed NaPSS chains seem to have a more elongated conformation than that for large NaPSS chains. This fact is emphasized in Figure 7 where an expansion factor α_t of the thickness of the adsorbed layer defined by the ratio of the thickness at the applied potential to that at the rest potential is plotted against ΔV. The expansion factor α_t at lower molecular weight NaPSS samples shows a steeper increase with negative ΔV than that of high molecular weight NaPSS. The value of α_t at constant negative ΔV increases with decreasing molecular weight of NaPSS.

On the other hand, at positive ΔV, the α_t value does not change so dramatically in comparison with that at negative ΔV and levels off to a constant value with increasing ΔV. This means that adsorbed NaPSS chains are not so much deformed at positive ΔV.

Plateau Thickness in Aqueous 0.1 M NaCl Solution. Figure 8 shows a double-logarithmic plot of the plateau thickness of the adsorbed layer against the molecular weight in aqueous 0.1 M NaCl solution, which corresponds to a good solvent for NaPSS. At the rest potential, the thickness of the adsorbed layer scales as $M_w^{0.4}$ and is comparable to the diameter of a NaPSS chain in bulk solution for low molecular weight, while for high molecular weight it is smaller than the diameter of a NaPSS chain. Thus, the molecular weight dependence of the thickness in a good solvent is weaker than that in a Θ solvent. The smaller exponent of molecular weight dependence of the adsorbed layer thickness than that in the Θ solvent is also found experimentally for nonionic polymers.[21,22] An attempt has been made to explain this in terms of a scaling form and agreement between experiments and theories was obtained.[21,22]

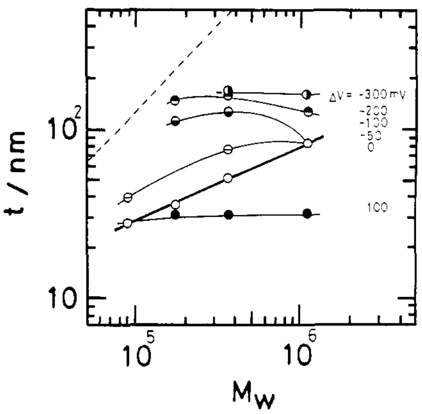

Figure 8. Double-logarithmic plot of adsorbed layer thickness versus molecular weight of NaPSS in aqueous 0.1 M NaCl solution. The number indicates the potential difference between applied and rest potentials. Dashed line corresponds to the contour length of a free NaPSS chain.

Cosgrove, Obey, and Vincent[11] recently have measured the hydrodynamic thickness of NaPSS adsorbed on polystyrene latex particles having negative or positive surface charges in aqueous NaCl solutions by using photon correlation spectroscopy and small-angle neutron scattering techniques as a function of molecular weight of NaPSS as well as ionic strength in bulk solution. Their experimental conditions correspond to a good solvent for NaPSS. The molecular weight dependence of the hydrodynamic thickness seems to scale as $M_w^{\sim 0.4}$, which can be estimated from their data. Moreover, they reported that the hydrodynamic thickness of NaPSS adsorbed on polystyrene latex surface increases with decreasing salt concentration and that its absolute value is smaller than the diameter of a NaPSS chain in bulk solution. Thus, the variation of the hydrodynamic thickness of NaPSS layer adsorbed on polystyrene latexes with salt concentration is similar with that for this experiment.

As seen in Figure 8, at a given potential difference the molecular weight dependence of the ellipsometric thickness of the adsorbed layer differs from that at the rest potential. Usually with increasing negative ΔV the thickness increases and its molecular weight dependence becomes weaker. Especially, the thickness of the adsorbed NaPSS-2 layer at $\Delta V = -200$ mV is close to the contour length; NaPSS-2 chains take a fairly stretched conformation at $\Delta V = -200$ mV. On the other hand, at positive ΔV the thickness decreases gradually with increasing ΔV and the exponent of the molecular weight dependence is approximately zero at $\Delta V = 100$ mV as seen from Figure 8. Large NaPSS chains undergo a stronger effect of the positive ΔV on the conformation change than small ones.

Figure 9 displays the effect of ΔV on α_t defined as the ratio of the thickness at the applied potential to that at the rest potential in a good solvent. The steep increase of α_t was observed for the lower molecular weight samples.

Conformation Changes of Adsorbed NaPSS Chains Due to Potential Differences. We now come to our proposal of a rather speculative model to understand the origin of the conformation changes of NaPSS chains under applied potential. The main origin, undoubtedly should reflect electrostatic repulsions or attractions between charges in chains and charges of surface. Applied potential induces some currents, thus it is expected that these currents, behaving as a kind of electrophoretic process, further influence the conformation changes of the adsorbed

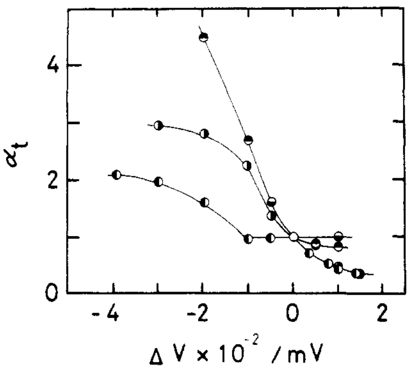

Figure 9. Expansion factor α_t in aqueous 0.1 M NaCl solution as a function of potential difference. Symbols are the same as in Figure 7.

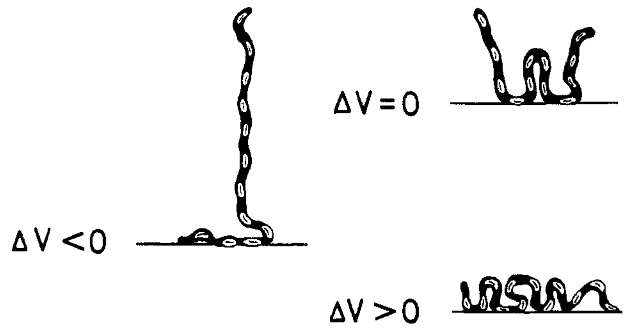

Figure 10. Models proposed for the conformation changes of a short adsorbed NaPSS chain under potential variation in a Θ-solvent condition.

polyelectrolyte chains. Our proposed model of the conformation of an adsorbed short chain to interpret the observed thickness under Θ-solvent conditions is shown in Figure 10. At negative ΔV a chain takes a more extended conformation with elongated tails. In contrast, at positive ΔV a chain is squeezed to make a flattened conformation with short loops and a number of trains. Thus, applied potentials are sufficient to deform adsorbed NaPSS molecules. Similar results for deformation of adsorbed polymer chains under impressed potentials were obtained for adsorption experiments of proteins onto platinum plate.[14]

Conclusions

Ellipsometric thicknesses of NaPSS chains adsorbed on the platinum plate strongly depend on the chain molecular weight and the potential difference, ΔV. At negative ΔV the molecular weight dependence of the thickness indicates a very different behavior from that at the rest potential. The exponent of molecular weight dependence of the thickness decreases with increasing negative ΔV and almost becomes zero above $\Delta V = -300$ mV. Especially the thickness of small NaPSS chain at high negative ΔV is comparable to the contour length of a free chain.

At positive ΔV a large NaPSS chain in a good solvent is strongly squeezed to form a flattened conformation and the absolute value of the thickness is nearly constant, independent of molecular weight.

Registry No. Pt, 7440-06-4.

References and Notes

(1) Hesselink, F. Th. *J. Colloid Interface Sci.* **1977**, *60*, 448.
(2) Marra, J.; van der Schee, H. A.; Fleer, G. J.; Lyklema, J. In *Adsorption from Solution*; Ottewill, R. H., Rochester, C. H., Eds.; Academic: London, 1984; p 245.
(3) van der Schee, H. A.; Lyklema, J. *J. Phys. Chem.* **1984**, *88*, 6661.
(4) Papenhuijzen, J.; van der Schee, H. A.; Fleer, G. J. *J. Colloid Interface Sci.* **1985**, *104*, 540.
(5) Pefferkon, E.; Dejardin, P.; Varoqui, R. *J. Colloid Interface Sci.* **1978**, *63*, 353.
(6) Gramain, Ph.; Myard, Ph. *J. Colloid Interface Sci.* **1981**, *84*, 114.
(7) Takahashi, A.; Kawaguchi, M.; Kato, T. *Polym. Sci. Technol.* **1980**, *12B*, 729.
(8) Takahashi, A.; Kawaguchi, M.; Hayashi, K.; Kato, T. In *Polymer Adsorption and Dispersion Stability*; Goddard, E. D., Vincent, B., Eds.; ACS Symposium Series 240; American Chemical Society: Washington, DC, 1984; p 39.
(9) Kawaguchi, M.; Hayashi, K.; Takakashi, A. *Macromolecules* **1984**, *17*, 2066.
(10) Luckham, P. F.; Klein, J. *J. Chem. Soc., Faraday Trans 1* **1984**, *80*, 865.
(11) Cosgrove, T.; Obey, T. M.; Vincent, B. *J. Colloid Interface Sci.* **1986**, *111*, 409.
(12) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(13) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982** *46*, 1.
(14) Morrissey, B. W.; Smith, L. E.; Stromberg, R. R.; Fenstermaker, C. A. *J. Colloid Interface Sci.* **1976**, *56*, 557.
(15) Liedberg, B.; Ivarsson, B.; Hegg, P. O.; Lundstrom, I. *J. Colloid Interface Sci.* **1986**, *114*, 386.
(16) Stromberg, R. R.; Tutas, D. J.; Passaglia, E. *J. Phys. Chem.* **1965**, *69*, 3955.
(17) Gebhard, H.; Killmann, E.; *Makromol. Chem.* **1976**, *53*, 171.
(18) Takahashi, A.; Kawaguchi, M.; Hirota, H.; Kato, T. *Macromolecules* **1980**, *13*, 884.
(19) Dejardin, P.; Varoqui, R. *J. Chem. Phys.* **1981**, *75*, 4115.
(20) Lee, J.-J.; Fuller, G. G. *Macromolecules* **1984**, *17*, 375.
(21) Kawaguchi, M.; Takahashi, A. *Macromolecules* **1983**, *16*, 1465.
(22) Klein, J.; Luckham, P. F. *Macromolecules* **1986**, *19*, 2007.