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Dynamics of Adsorbed Polymers. 1. Thickness Relaxation of Poly(vinylpyrrolidone) on Glass

Martinus A. Cohen Stuart* and Hisashi Tamai†

Laboratory for Physical and Colloid Chemistry, De Dreijen 6, 6703 BC Wageningen,
The Netherlands, and Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Shitami Saijō-chō, Higashihiroshima-city, 724 Japan.
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ABSTRACT: We present kinetic data that give a rather direct insight into the time scale of rearrangement processes occurring inside an adsorbed polymer layer. In particular, we were able to measure the hydrodynamic thickness of a freshly deposited adsorption layer as a function of time, and we found it to decrease over a time of the order of minutes. We present data for this relaxation process, which show that it is not simply exponential and that it strongly depends on the thickness increment prior to relaxation. We also present data on the relaxed thickness as a function of the number of deposition steps, polymer concentration, and molecular weight. The results can be qualitatively understood in terms of a simple two-stage adsorption.

Introduction

Static properties of adsorbed polymers have received much attention over more than 2 decades. As a result of numerous efforts there is now a considerable body of detailed knowledge, both theoretical and experimental. The state of the art has been discussed in recent reviews.[1,2]

Dynamic properties, on the other hand, are largely unknown. In some cases, a measured property, e.g., adsorbed amount or surface pressure, has been reported as a function of time,[3-5] but the number of systematic studies is small. Some careful kinetic studies were carried out in Strassbourg, both on the overall kinetics[6,7] and on the kinetics of exchange between adsorbed and free molecules in a saturated adsorption layer.[8] Rheological properties of polymers at fluid interfaces have been studied,[9] and it has been proposed that such layers may have glasslike properties under suitable conditions.[10,11] A kinetic theory for exchange with a saturated layer was proposed.[12]

A very characteristic aspect of polymer adsorption is the change in conformation that molecules must undergo to minimize the free energy. Since the rearrangement processes that must lead to equilibrium conformations are an essential aspect of the adsorption process, it would be interesting to have some information on the time scales involved. However, such information cannot easily be extracted from studies published so far, since these studies dealt with situations where the adsorbent surface was continuously in contact with a polymer solution of finite concentration. Under such conditions, transport by diffusion and conformational rearrangement occur simultaneously, and the two processes can be separated only with the help of a theoretical model. Such approaches provide, at best, circumstantial evidence.

Table I
PVP Polymer Samples

sample	$10^3[\eta]$, dm^3 g^{-1}	M_w, g mol^{-1}
K-17	7.8	8900
K-30	22.2	43000
K-30$_{\mathrm{III}}$	40.5	102000
K-90	160.4	731000
K-90$_{\mathrm{III}}$	76.5	254000

We therefore took a different approach. First of all, we decided to study the hydrodynamic thickness of adsorption layers during their formation, since from earlier work[13,14] we expected this quantity to the rather sensitive to conformational rearrangement. A polymer molecule that just starts to adsorb is still dilute and would stick out far into the solution, thus contributing strongly to the hydrodynamic thickness. As the chain is gradually pulled inward, we expect the thickness to decrease. In earlier work, we have shown that for uncharged polymers adsorbing from aqueous solution, the hydrodynamic layer thickness can be accurately measured by means of electrokinetic (preferably streaming potential) measurements at low ionic strength, especially if the layer thickness is not too large.[13] We therefore adopted this technique.

Second, we decided to study the rearrangement process in isolation, by suppressing polymer transport from the solution to the interface. This calls for an instantaneous removal of free molecules from the system. In our setup the adsorption occurs at the inner wall of a capillary that is continuously flushed with an aqueous electrolyte solution. Jumps between zero and finite polymer concentration can be easily achieved by pulsewise injection of polymer solution into the flowing electrolyte.

Experimental Section

Materials. Commercially available poly(vinylpyrrolidone) (PVP, Kollidon from BASF) was used. Three rather polydisperse samples (K-17, K-30, and K-90) of different molecular weight and

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* To whom correspondence should be addressed at the Laboratory for Physical and Colloid Chemistry.
† Hiroshima University.

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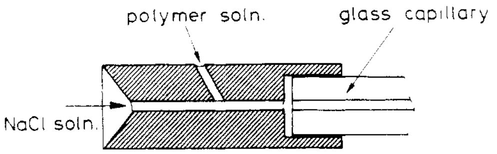

Figure 1. Polymer solution injection device.

two of their fractions (K-30_{III} and K-90_{III}) prepared by fractional precipitation from acetone–water mixtures were used. The viscosity-averaged molecular weights are shown in Table I. The viscosity was measured by using an Ubbelohde viscometer.

All other chemicals were of Analar grade, and water was purified by filtration through a Millipore Milli R060 combined with a Super Q system.

Streaming Potential Measurements. Glass capillaries of 21-cm length and having an i.d. of approximately 0.4 mm were used throughout the experiment. Prior to each measurement, capillaries were cleaned by subsequently soaking in sulfochromic acid and in 2 N nitric acid for at least 24 h. Capillaries were then immersed in 10^{-1} M NaOH solution and washed in water.. This procedure leads to clean, hydrophilic glass surfaces that behave reproducibly under the adsorption experiments carried out by us.

A glass capillary was mounted between two containers with electrolyte solution, and a specially developed Teflon injection piece connected to a motor buret containing polymer solution was installed. The experimental setup is schematically shown in Figure 1. Streaming potentials were measured with platinum black electrodes connected to a Fluke 8022 A multimeter. The electrolyte was 10^{-3} M NaCl throughout.

An adsorption experiment was carried out in steps by repeatedly injecting a polymer solution for a short period of time (10–80 s) into the flowing electrolyte while continuously monitoring the streaming potential. If not stated otherwise, the applied pressure was 30 cmHg, the average flow rate 0.174 mL s^{-1}, and the injection rate for the polymer solution 0.05 mL s^{-1}.

The streaming potential of the glass capillaries was reduced due to the adsorption of polymer. This reduction can be interpreted as due to an effective outward displacement of the slipping plane. This relation has been studied in detail by several authors.[13-17] It can be shown that under suitable conditions the hydrodynamic thickness δ_H is directly obtained from the streaming potential by using

$$\delta_H = \kappa^{-1} \ln (V_{s,o}/V_{s,p})$$

where κ^{-1} is the Debye screening length (10 nm in the present case) and $V_{s,o}$ and $V_{s,p}$ are the streaming potentials in the absence and in the presence of an adsorbed layer, respectively.

The equation is valid for relatively thin adsorption layers ($\kappa\delta_H < 1$), a negligible perturbation of the static double layer due to the polymer, and absence of surface conduction effects. As these conditions were found to apply,[14] we continuously used this simple equation. It should be noted, however, that *saturated* layers may be considerable thicker.[14]

Results and Discussion

Typical data are shown in Figure 2, where we plot both V_s and δ_H as a function of time as well as a schematic diagram showing polymer injections. Under the conditions of the experiment $V_{s,o}$ equals −275 ± 1 mV. As can be seen, V_s decreases steeply during an injection but thereafter gradually increases. After some time, V_s has relaxed to a new steady-state value, with a corresponding *relaxed* thickness that we shall denote as $\bar{\delta}_H$. The layer thickness can then be further increased by a second, third, etc., injection. It should be said at the outset that the results to be discussed correspond in most cases to strongly unsaturated, thin, and unrelaxed adsorption layers, because only a very small fraction of the polymer injected is actually adsorbed. Most experimental studies so far (e.g., ref 14 and 15) deal with saturated (i.e., in contact with an equilibrium solution of finite concentration) rather thick and fully relaxed layers. From these studies and from theoretical work (see also ref 1) it is known that equilibrium thicknesses for a given polymer/solvent/substrate system depend only on the adsorbed amount and, therefore, only indirectly on molecular weight. Moreover, for thick layers, there is much evidence that δ_H is mainly determined by the extension of "tails".

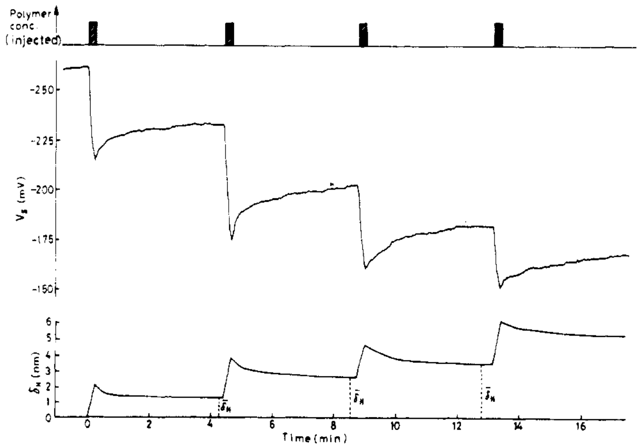

Figure 2. Streaming potential (V_s), hydrodynamic thickness (δ_H), and polymer concentration as a function of time during a typical experiment: shaded area, injection of polymer; polymer K-30_{III}, 40 mg dm^{-3}; injection rate, 0.05 mL s^{-1}; injection time, 10 s.

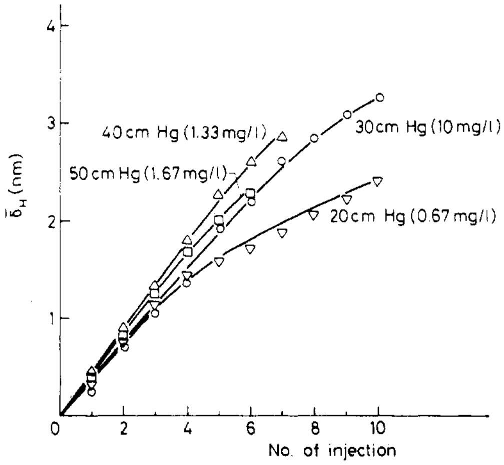

Figure 3. Influence of pressure drop on $\bar{\delta}_H$: polymer K-30_{III}, concentrations as indicated; injection rate, 0.05 mL s^{-1}; injection time, 10 s.

For the adsorption layers we study here, only the relaxed thickness $\bar{\delta}_H$ may be expected to depend unambiguously on the adsorbed amount. However, this dependence is unknown. Furthermore, the layers are usually thin, and (long) tails would not seem to be important.

Before we ascribe results as shown in Figure 2 entirely to intrinsic processes of the adsorption layer, we have to verify that the fact that the adsorbed layer is exposed to a flow field has no consequence. We therefore carried out two checks. First, we measured $V_{s,p}$ at two points on the relaxation curve separated by several minutes during which we reduced the pressure drop to zero. The result was the same as that obtained during continuous solvent flow. This proves that the decrease in thickness is not due to flow enhanced desorption. Flow enhanced desorption is, indeed, observed only for very thick adsorption layers consisting of very high molecular weight polymer molecules.[18] Our conclusion is further substantiated by results presented in Figure 3, where we compare the relaxed thickness $\bar{\delta}_H$ as a function of the number of injections, obtained for pressures varying between 20 and 50 cmHg.

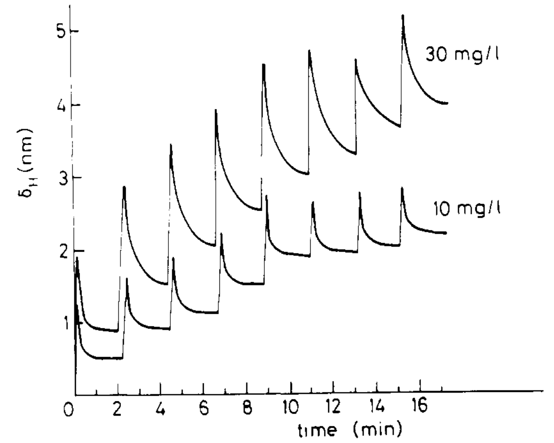

Figure 4. Effect of repeated injections on $\bar{\delta}_H$ for two different concentrations: polymer K-30$_{III}$; injection rate, 0.05 mL s^{-1}; injection time, 10 s.

For the polymer concentration in the capillary to be kept constant, the injected concentration had to be varied in the same proportions. As can be seen, the thickness $\bar{\delta}_H$ shows little and certainly not systematic variation with pressure at least up to three–four injections. Desorption due to flow therefore seems unlikely. (We attribute the differences in Figure 3 for 20 cmHg and more than four injections to variations in the mixing pattern and therefore to the effective concentration near the adsorbent wall.) It is concluded that between injections, the adsorbed amount is constant.

The next question is whether the adsorbed polymer is deposited homogeneously over the available surface or whether adsorption has taken place mainly at the inlet side of the capillary. Two reasons make the latter case rather unlikely. First, had adsorption occurred only at one end of the capillary, the resulting streaming current would have been dominated by the bare surface contribution, and since the capillary is too wide for surface conduction to play a role, V_s would hardly have been affected. This is not what is observed. Second, the flow rates is so high that convective transport can easily maintain a constant polymer concentration up to very close to the wall. It therefore seems very unlikely that the rate of adsorption decreases in the downstream direction as a result of depletion.

Figure 4 shows δ_H versus t curves obtained for two series of eight injections each, differing only in polymer concentration (10 and 30 mg L^{-1}, respectively). Two observations can be made:

(1) The increase (during 10-s injections) is higher at higher bulk concentrations; this is obviously due to the material flux toward the interface being higher at higher concentration.

(2) The relaxation curves are different for the two series: at 10 mg L^{-1} there is a rapid decrease of the order of 0.75 nm in less than 1 min; at 30 mg L^{-1} the relaxation covers about 1.5 nm but is much more gradual and extends over longer times (>3 min). It would seem that the thickness increment during an injection determines the relaxation pattern.

Adsorbed mass and thickness increment can be increased not only by increasing concentration but also by making the injection time longer. This is borne out by results in Figure 5, where we adsorbed polymer on an initially bare wall during injections varying in duration from 10 to 80 s. We observe that after a short injection, relaxation is again rapid (20–40 s), whereas the longest injection requires at least 4 min to relax fully. It should also be noted, that the thickness increase during the injection period is nonlinear; this seems to imply that the rate of deposition slows down. The fact that the initial deposition has a marked effect on the relaxation rate is indicative of competition: the relaxation paths available to the system have finite capacity.

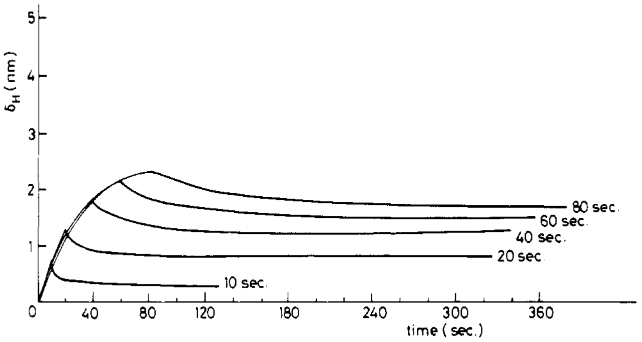

Figure 5. Influence of injection time on relaxation behavior: polymer K-30$_{III}$, 10 mg dm^{-3}; injection rate, 0.05 mL s^{-1}.

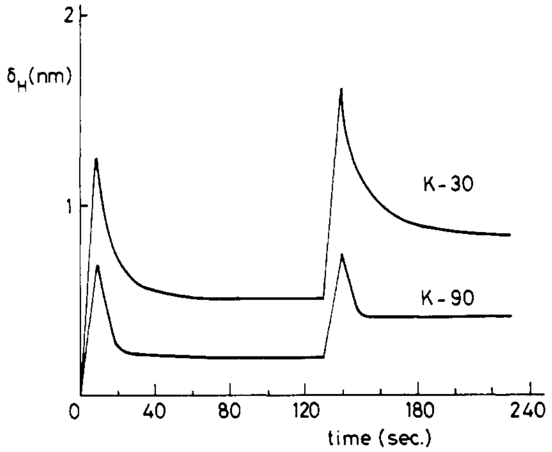

Figure 6. Influence of molecular weight on relaxation behavior: injection rate, 0.05 mL s^{-1}; injection time, 10 s; molecular weight given in Table I.

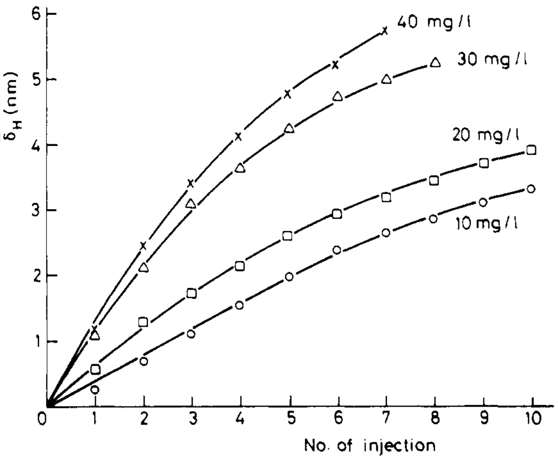

Figure 7. Effect of injected polymer concentration on $\bar{\delta}_H$: polymer K-30$_{III}$; injection rate, 0.05 mL s^{-1}; injection time, 10 s.

An interesting variable is the molecular weight. One might speculate that higher molecular weight molecules need more time to relax. To check this we compare in Figure 6 δ_H versus t curves for two molecular weights (K-30 and K-90, respectively) under otherwise similar conditions. The result, however, is more like those in Figure 4, where a concentration effect was observed. The higher MW K-90 sample increases more slowly than does K-30, and the thickness increase after the 10 s of injection is smaller.

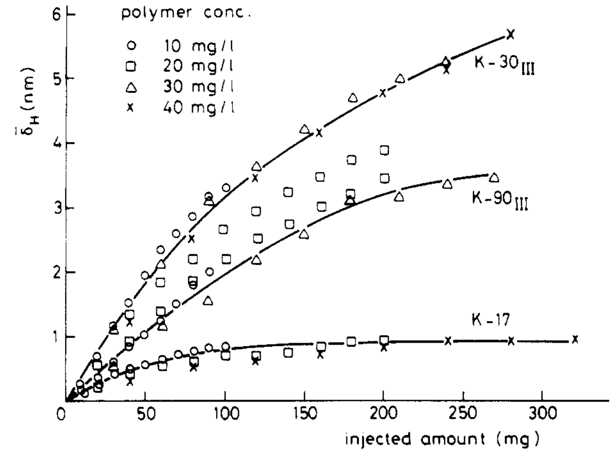

Figure 8. Effect of injected amount on $\bar{\delta}_H$, for various molecular weights: injection rate, 0.05 mL s^{-1}; injection time, 10 s.

This seems consistent with a lower diffusion coefficient for K-90; an estimate on the basis of M_w of the samples would lead to a factor that would agree with our observation. The relaxation rate is, again, slower at higher depositions and not at higher molecular weight.

Figure 7 summarizes a number of data for $\bar{\delta}_H$, plotted as a function of the number of injections, for four different concentrations of the injected polymer solution. At low concentrations, $\bar{\delta}_H$ increases almost linearly for the first six–seven injections, (about 0.4 nm per injection) corresponding to a total thickness of ~2.5 nm. For thicker layers a deviation from linearity appears. At higher concentrations, the thickness increases faster. A remarkable result is that all the curves can be made to coincide when plotted as a function of the injected amount (i.e., $\sim\sum c_i t_i$ at constant injection rate). This is shown in Figure 8, where $\bar{\delta}_H$ is plotted for three molecular weights. The same layer thickness is found for a few injections at high concentration and more injections at low concentration, provided $\sum c_i t_i$ is the same. This seems to imply that the deposition rate is nearly constant in time and only dependent on c during these measurements.

A more surprising result is that $\bar{\delta}_H$ as a function of molecular weight has a maximum. The lowest molecular weight sample K-17 forms a layer that is apparently already saturated at 1 nm. This is consistent with earlier results.[14] For K-30 we find a rapid increase; from previous studies we expected a leveling off (at 10^{-3} M NaCl) around 9 nm, which is beyond the present range. However the highest molecular weight (K-90) definitely increases much slower, although we know that it must saturate around 27 nm.[14] We tend to ascribe this to a smaller diffusion coefficient for K-90, but this is rather speculative.

In an attempt to rationalize the data presented here, we suggest the following mechanism. Within the polymer layer we distinguish between two zones: a dense, fully relaxed zone adjacent to the substrate, and a loose, nonrelaxed zone on the solution side. The nonrelaxed zone has a finite capacity, and hence the rate of deposition will slow down after some deposition has occurred. Meanwhile, molecules pass from the nonrelaxed to the relaxed state with a "relaxation rate" that also depends on the population of the "nonrelaxed" state. As we pointed out above, we observe a slowing down of the relaxation rate, probably due to competition. On the basis of this model, we therefore expect that for a surface that is continuously in contact with a polymer solution, the initial thickness increase will be governed by diffusion-controlled deposition, but after some time a steady state is reached, where the slow relaxation rate becomes entirely rate controlling.

Conclusion

We have shown that an injection technique, combined with electrokinetic measurements of the hydrodynamic thickness, enables us to follow relaxation processes inside an adsorbed polymer layer. The relaxation rate decreases strongly with increasing amount of polymer on the wall in a nonrelaxed conformation. The effect of molecular weight on the relaxation rate seems to be minor, but high molecular weights appear to adsorb slower probably because of a slower diffusion.

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