(7) Miller, R. L.; Boyer, R. F. *Polym. News* 1978, *4*, 255.
(8) Miller, R. L. MMI unpublished collection of cross-section areas per chain.
(9) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980; Table 12-III, pp 330–331.
(10) Boyer, R. F. *Macromolecules* 1981, *14*, 376.
(11) Boyer, R. F. *Colloid Polym. Sci.* 1980, *258*, 760.
(12) Boyer, R. F. *Macromolecules* 1982, *15*, 774.
(13) Šolc, K.; Keinath, S. E.; Boyer, R. F. *Macromolecules* 1983, *16*, 1645.
(14) Boyer, R. F. *Macromolecules* 1982, *15*, 1498.
(15) Boyer, R. F. *Polym. Eng. Sci.* 1979, *19*, 732.
(16) Boyer, R. F. *J. Macromol. Sci., Phys.* 1980, *B18*, 461.
(17) Boyer, R. F. *Eur. Polym. J.* 1981, *17*, 661.
(18) Lobanov, A. M.; Frenkel, S. Ya. *Polym. Sci. USSR (Engl. Transl.)* 1980, *22*, 1150. Also: *Vysokomol. Soedin.* 1980, *22*, 1045.
(19) Boyer, R. F.; Heeschen, J. P.; Gillham, J. K. *J. Polym. Sci., Polym. Phys. Ed.* 1981, *19*, 13.
(20) Passaglia, E.; Martin, G. M. *J. Res. Natl. Bur. Stand., Sect. A* 1964, *68*, 273.
(21) Wood, L. A.; Martin, G. M. *J. Res. Natl. Bur. Stand., Sect. A* 1964, *68*, 259.
(22) Gee, G. *Polymer* 1966, *7*, 177.
(23) Olabisi, O.; Simha, R. *Macromolecules* 1975, *8*, 206.
(24) Beret, S.; Prausnitz, J. M. *Macromolecules* 1975, *8*, 536.
(25) (a) Barlow, J. W. *Polym. Eng. Sci.* 1978, *18*, 238. Dr. Barlow provided us with additional data and facts not given in the above reference. (b) Private communication from Dr. Barlow.
(26) Kraus, G.; Childers, C. W.; Gruver, J. T. *J. Appl. Polym. Sci.* 1967, *11*, 1581. These authors provide a method of calculating T_g for mixed isomers of PBD.
(27) Jain, R. K.; Simha, R. *Polym. Eng. Sci.* 1979, *19*, 845.
(28) (a) Miller, R. L.; Boyer, R. F.; Heijboer, J. *J. Polym. Sci., Polym. Phys. Ed.*, in press. (b) Miller, R. L.; Boyer, R. F. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(29) Miller, R. L.; Boyer, R. F. *Bull. Am. Phys. Soc.* 1978, *23*, 371 (Abstract GZ-3).
(30) Simha, R.; Boyer, R. F. *J. Chem. Phys.* 1962, *37*, 1003.
(31) Boyer, R. F.; Miller, R. L., unpublished observations.
(32) Miller, R. L. In "Polymer Handbook", 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; section III.
(33) Quach, A.; Wilson, P. S.; Simha, R. *J. Macromol. Sci., Phys.* 1974, *B9*, 533.
(34) Boyer, R. F., unpublished studies on T_{ll} in PS and PoMS from isothermal *V–P* data.
(35) Oels, H.-J.; Rehage, G. *Macromolecules* 1977, *10*, 1036. Tabulated data provided by Prof. G. Rehage, University of Clausthal, West Germany.
(36) Loomis, L. D.; Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* 1983, *21*, 241.
(37) Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* 1982, *20*, 1533.

Effect of Polyelectrolytes on the Rate of Ligand–Metal Ion Reactions. 3. Role of Hydrophobic Interactions between Ligand and Polyelectrolyte

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ABSTRACT: The part played by the hydrophobic interactions in the polyelectrolyte "catalysis" of some ligand–metal ion (Ni(II) and Co(II)) complex formation is investigated (i) by changing the substituent groups of the ligand (pyridylazo compound) and (ii) by using as polyelectrolytes, copolymers of methacrylic acid and styrene with varying amounts of styrene. The maximum "catalysis" effect is shown to be very dependent on the hydrophobic character of both the ligand and the polyelectrolyte. The polyelectrolyte concentration giving the maximum effect is generally related to the complete condensation of divalent ions as can be predicted from Manning's theory, whereas the amplitude of the effect is related to the strength of the hydrophobic interaction between the ligand and the polyelectrolyte. An improved model is proposed on the basis of the present results to interpret the acceleration effect of hydrophobic polyelectrolytes.

Introduction

Since the pioneering work of Morawetz and co-workers,[1-4] the polyelectrolyte "catalysis" of chemical reactions involving ionic species has been the object of numerous papers in the last years[5-34] (the list given in References and Notes is far from being exhaustive).

Some applications of such a property of charged polymers have also been put forward dealing with the possibility of performing the necessary charge separation in photoelectron-transfer reactions where hydrogen production is expected.[35-37] The mechanisms responsible for the effect of polyelectrolytes are complex and their complete understanding calls for new experiments.

Extensive work on this subject has been particularly performed by Ise and co-workers,[5-23] who have added new insight to this field by investigating the role of solvation and desolvation of the reactants and activated complexes.[16-23]

For our part, we have been concerned in previous papers with the effects of polyanions on some complexation reactions between a pyridylazo ligand and divalent transition-metal ions.[31-33] A rate-accelerating effect has been shown to occur in the presence of sodium poly(styrenesulfonate)[31,32] whereas a rate-retarding effect occurs with sodium polyphosphate.[31,33] As both polyelectrolytes are of the anionic type and, furthermore, are characterized by the same charge parameter, there was no possible interpretation without taking into account specific interactions between the divalent metal ion and the polyanion on the one hand and the hydrophobic interactions between the ligand and the polymer when they may occur, on the other hand.

The purpose of the present investigation is to define the part played by the hydrophobic interactions. Two different approaches have been considered: (i) the influence of the hydrophobic character of the ligand has been investigated by changing the substituent groups of the pyridylazo radical; (ii) the influence of the hydrophobic character of the polyelectrolyte has been studied by using copolymers of methacrylic acid and styrene with varying amounts of styrene.

Experimental Section

Materials. The pyridylazo compounds obtained from the following sources were used without further purification: *N,N*-dimethyl-4-(2-pyridylazo)aniline (PADA) from Sigma, 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-pyridylazo)-2-naphthol (β-PAN) from Fluka. Stock solutions of concentration 2.5×10^{-4} M were prepared in water acidified with HCl for PADA and PAR

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and in a 50/50 (v/v) water–dioxane mixture for β-PAN.

The Co(II) and Ni(II) salts used were of analytical grade and their water content was checked by complexometry with EDTA.

The sodium poly(styrenesulfonate) (PSS-Na) was a commercial sample VERSA-TL 500 from Proctor Chemical Co., of molecular weight 500000 (kindly supplied by Dr. C. D. Czymanski). It was carefully purified following a previously described procedure.[38] The styrene–methacrylic acid copolymers (STYR-MA) were prepared according to the procedure described in ref 39. The polymerization was performed in tetrahydrofuran with azobis(isobutyronitrile) as initiator. The elementary analysis of these samples indicated styrene content of respectively 34.8 and 17.8 mol%. These results were confirmed at better than 1% by a titration of carboxylic functions in dimethylformamide.[39] Further purification of these copolymers has been carried out by a classical dissolution/precipitation procedure two times repeated in the couple methanol/ether. The final products showed a slight decrease in styrene content respectively of 32% (STYR-MA 32) and 12% (STYR-MA 12). The sodium salts of these copolymers were obtained from a stoichiometric neutralization of the carboxylic functions by sodium hydroxide.

The poly(methacrylic acid) sample (PMA) was a fraction of molecular weight 270000, of the same origin as in a previous paper.[38]

Kinetic Measurements. The kinetic measurements were performed with a stopped-flow spectrophotometer with a 2-cm optical path. The apparatus was essentially a Durrum D110 model, except that the optical part was a Unicam SP500 UV–visible spectrometer, which replaced the original monochromator and lamp assemblies. The on-line acquisition of kinetic data and treatment with a nonlinear least-squares procedure were performed with the aid of a NM 4/30 Computerautomation computer equipped with a Regent 40 terminal display, Centronic 702 line printer, Tektronix 4662 digital plotter, and a Biomation 805 transient recorder.

The ligand and polyelectrolyte were equilibrated in the same syringe, the divalent metal ion solution being in the other syringe. As buffers were avoided because of their possible interference with the system studied, the pH of the solutions before mixing had to be adjusted with sodium hydroxide so as to lead to the chosen final value, which was checked by collecting the reaction products at the exit of the optical cell. All concentrations given are concentrations after mixing the two solutions in equal volumes.

The ligand concentration was always kept very small (1.25×10^{-5} M) compared to the divalent metal ion concentrations (10^{-3} M) in order to ensure pseudo-first-order conditions. Pseudo-first-order rate constants k_{obsd} were then obtained from the exponential change of the absorbance at the wavelength characterizing the metal–ligand complex ($k_{obsd} = 1/\tau$, with τ being the computed relaxation time of the exponential). Each point in the figures is usually an average over at least four experiments.

In some instances the results could not be properly fitted with a single exponential, and a function with a sum of two exponentials was used in place in the least-squares procedure. This was particularly the case for the ligands PAR and PAN which can form 1:1 and 2:1 ligand:metal complexes.[40] The corresponding rates of formation are usually well separated on the time scale, and the results reported here are always relative to the fastest relaxation time, which is presumably related to the 1:1 complex formation. As already mentioned,[32] in the case of PADA with PSS-Na at low polyelectrolyte concentration, a better fit of the kinetic curve is obtained when two relaxation times are considered, the main process (fastest relaxation time and largest amplitude) being followed by a second relaxation time of small amplitude. The mechanism responsible for this last relaxation time is not clearly identified yet, but it seems to be related to the polyelectrolyte–ligand interaction. Nevertheless the single exponential fit gave a value of τ close to that obtained for the main process, and only this relaxation time will be considered.

Results and Discussion

"Catalysis" of Pyridylazo Ligand–Divalent Metal Ion Complex Formation by PSS-Na: Influence of the Hydrophobicity of the Ligand. The idea was to use ligands with the same basic chemical structure but with different substituent groups R changing the hydrophobic character of the ligand and thus its affinity for the polyelectrolyte.

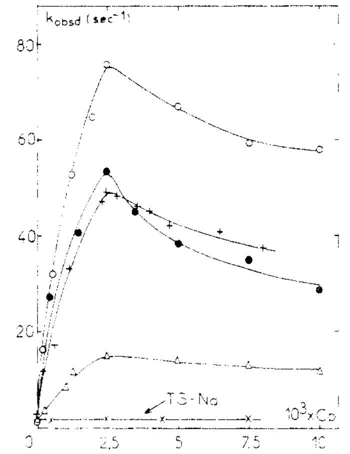
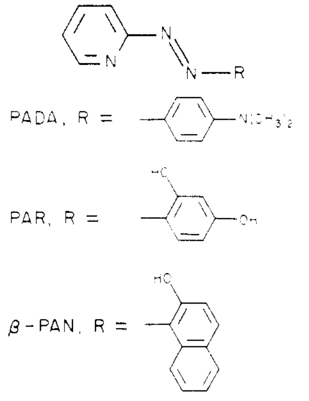


Figure 1. Influence of PSS-Na and TS-Na on some ligand–Me^{2+} reactions at 25 °C. C_P is the polyelectrolyte concentration in mol of monomeric residues/L ($[Me^{2+}] = 10^{-3}$ M, [ligand] = 1.25×10^{-5} M): PADA–Ni^{2+} at pH 7 ± 0.5 in H_2O (○) and in H_2O–5% dioxane (●); PAR–Ni^{2+} at pH 5 ± 0.5 in H_2O (△); β-PAN–Co^{2+} at pH 5 ± 0.5 in H_2O–5% dioxane (+).



The hydrophobic character of these compounds in their neutral (uncharged) form is expected to increase in the order β-PAN > PADA > PAR, that is inversely to their solubility in water. β-PAN is so poorly soluble in water that the presence of an organic solvent is necessary, and experiments with this ligand were performed in H_2O–5% dioxane as was previously done by others.[40] All three compounds can form complexes with Ni^{2+} or Co^{2+} ions, and some results exist in the literature concerning the kinetics of complex formation in the absence of polyelectrolytes.[40–45] The kinetics are known to be much faster for the complexation of Co^{2+} compared to Ni^{2+}, the reason being the large difference in the rate of water exchange.[46] On the other hand, for a chosen metal ion, the kinetics of complexation with PADA and PAR takes place on a very comparable time scale, whereas it is much slower (by more than an order of magnitude) for β-PAN[42] (it has been suggested that it may be due to the slow rotation of the bulky naphthol group, the hydroxyl of which is involved in the complex formation[40]). For this reason, experiments using the same technique were not easy to perform with the same metal ion, and we were led to use Ni^{2+} with PADA and PAR and Co^{2+} with β-PAN.

The results obtained with these different systems in the presence of increasing amounts of PSS-Na are represented in Figure 1. The p*K*'s were chosen so that the different ligands can be assumed to be mainly in a neutral form. Also represented in the same figure are the results obtained when the PADA–Ni^{2+} reaction takes place in H_2O–5%

Table I[a]

ligand	solvent	Me^{2+}	polyelectrolyte	pH (±0.5)	k^0_{obsd}, s^{-1}	k_{obsd}, s^{-1}	k_{obsd}/k^0_{obsd}	ref
PADA	water	Ni^{2+}	PP-Na	7	1.25 (±0.15)	0.1	0.08	32
			PSS-Na	7	1.25 (±0.15)	76	60.8	32
			Cop(STYR-MA 32)	7	1.25 (±0.15)	95	76	this work
				8.5	1.25 (±0.15)	102	81.6	
			Cop(STYR-MA 12)	7	1.25 (±0.15)	24.5	19.6	
			Cop(STYR-MalAc)	7	1.25 (±0.15)	13.4	10.7	32
			Cop(ET-MalAc)	7	1.25 (±0.15)	3.0	2.4	32
			Cop(MVE-MalAc)	7	1.25 (±0.15)	1.3	1.04	32
			PMA	7	1.25 (±0.15)	3.4	2.72	this work
PADA	water–5% dioxane	Ni^{2+}	PSS-Na	7	1.1	53.6	48.7	
PADA	water	Co^{2+}	PP-Na	7	100	9.6	0.096	33
PAR	water	Ni^{2+}	PSS-Na	5	1.8	14.5	8.05	this work
				7	5.3	0.8	0.15	
		Co^{2+}	PP-Na	5	67.1	1.5	0.022	
β-PAN	water–5% dioxane	Co^{2+}	PSS-Na	5	2.8	49	17.5	this work

[a] k^0_{obsd} and k_{obsd} are respectively the rates of ligand–Me^{2+} complex formation at 25 °C in the absence of polyelectrolyte and at the maximum (cases of acceleration) or minimum (cases of retardation) effect in the presence of polyelectrolyte. The ratio k_{obsd}/k^0_{obsd} is the corresponding acceleration or retardation factor. Abbreviations used are given in the text except PP-Na = sodium polyphosphate, Cop(STYR-MalAc), ET-MalAc, and MVE-MalAc = copolymers of maleic acid with styrene, ethylene, and methyl vinyl ether, respectively.

dioxane and is performed in the presence of sodium p-toluenesulfonate (TS-Na) in place of PSS-Na (TS-Na can be considered to be representative of a monomeric residue of PSS-Na; it has absolutely no influence on the rate of complexation of PADA–Ni^{2+} at concentrations where PSS-Na is quite effective). One can notice that an accelerating effect is observed for all the experiments in the presence of PSS-Na, the maximum of k_{obsd} occurring always for the same concentration of polyelectrolyte. The maximum accelerating effect observed for the PAR–Ni^{2+} is less than one-sixth of the effect observed for PADA–Ni^{2+}. On the other hand, comparable maximum rates are observed for PADA–Ni^{2+} and β-PAN–Co^{2+}, both of them in H_2O–5% dioxane.

The effect of pH on the reaction rate at the maximum is very important for the PAR–Ni^{2+} system, whereas for β-PAN–Co^{2+}, which is assumed to exist in a neutral form in a large domain of pH,[47] we have not observed any change between pH 4 and 8. (In the case of PADA–Ni^{2+} a sigmoidal change of k_{obsd} when increasing the pH has been previously reported and discussed.[32]) Thus, in the case of PAR–Ni^{2+} an accelerating effect is observed at pH ~5 whereas a retarding effect exists at pH 7; this is represented in Figure 2 in which the insert indicates the ionization states of the ligand depending on the pH according to the pK values given in ref 49. Similar inhibition curves have also been obtained for PADA–Ni^{2+},[31,32] PADA–Co^{2+},[33] and PAR–Co^{2+} (see Table I) in the presence of sodium polyphosphate (PP-Na), but the mechanism responsible for it is expected to be different in these cases.

An activation energy has been obtained from the temperature dependence of k_{obsd} for β-PAN–Co^{2+} (at maximum catalysis) and compared to the value obtained in the absence of PSS-Na; $\Delta H^{\ddagger}$ was respectively 38.8 and 45.6 kJ mol^{-1}.

"Catalysis" of PADA-Ni^{2+} Complex Formation: Influence of the Hydrophobicity of the Polyelectrolyte. We have seen above that PSS-Na shows an accelerating effect on the PADA-Ni^{2+} reaction. Another sytrene containing polyelectrolyte (an alternating copolymer of styrene and maleic acid (STYR-MalAc)) was previously shown to accelerate this reaction too[32] although with a lesser efficiency. We have thought to study more precisely the influence of the hydrophobic character of the polyelectrolyte by choosing a series of polymers with variable styrene content, the styrene residues being statistically distributed between methacrylic acid residues. Thus we have always the same charged groups interacting with the divalent ion, only the frequency of styrene units inside the chain being changed. The results obtained with two styrene–methacrylic acid copolymers with respectively 32 and 12% styrene units are compared with the result obtained for the homopoly(methacrylic acid) itself (0% styrene units) in Figure 3.

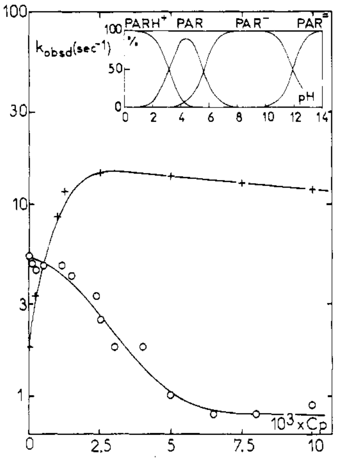


Figure 2. Influence of PSS-Na on PAR–Ni^{2+} reaction at 25 °C in H_2O ([Me^{2+}] = 10^{-3} M, [PAR] = 1.25×10^{-5} M): pH 5 ± 0.5 (+), pH 7 ± 0.5 (○). C_P is the polyelectrolyte concentration in mol of monomeric residues/L. The insert indicates the degree of the different forms of the ligand present vs. the pH according to the pK values given in ref 49.

On the contrary to the situation existing with a strong polyacid like PSS-Na, the charge parameter characterizing the polyelectrolyte depends on the pH. For this reason we have independently determined the titration curves giving the neutralization degree vs. pH and thus allowing the calculation of the mean charge parameter of each polyelectrolyte at a chosen pH.

The change of k_{obsd} with the polyelectrolyte concentration expressed in moles of ionizable groups/liter is illustrated in Figure 3. The three polymers have been studied at pH 7. A detailed investigation of the influence of the pH has been performed for the STYR-MA 32; at a fixed polyelectrolyte concentration, 6×10^{-3} mol of ionizable groups/L (i.e., the concentration giving the maximum catalysis at pH 7), k_{obsd} shows a maximum at around pH

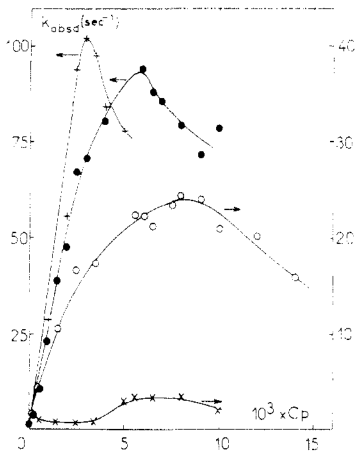


Figure 3. Influence of STYR-MA copolymers and PMA on PADA–Ni^{2+} reaction at 25 °C in H_2O: STYR-MA 32% pH 7 ± 0.5 (●) and pH 8.5 ± 0.5 (+); STYR-MA 12% pH 7 ± 0.5 (○); PMA homopolymer pH 7 ± 0.5 (x). C_P is the polyelectrolyte concentration in mol of ionizable groups/L.

7.5 and a drastic decrease at pH 6, where the polyelectrolyte is poorly ionized (under pH 6 the ionization is no longer sufficient to ensure the solubilization of the copolymer). The maximum catalytic effect obtained at pH 8.5 is occurring at a smaller polyelectrolyte concentration than that at pH 7, and the effect is slightly larger as also shown in Figure 3.

In addition one can notice that, even when the same pH is used, the maximum is occurring at a different polyelectrolyte concentration; for STYR-MA 12 the maximum is displaced toward higher polymer concentration. The effect of the hydrophobic character of the polyelectrolyte is perfectly clear: the higher the styrene content, the higher the catalytic effect observed for the same concentration of carboxylic groups is. The total elimination of styrene groups brings about practically a vanishing of the catalytic effect (case of PMA).

The effect of temperature has been studied in the conditions of concentrations giving the maximum effect for STYR-MA 32 at pH 8.5 (the effect is even larger than the effect previously reported for PSS-Na). The activation energy determined from the slope of the Arrhenius plot is $\Delta H^{\ddagger} = 46.5$ kJ mol^{-1}.

Ternary complexes of a polyelectrolyte–metal ion–simple ligand can serve as model systems for studying enzyme–substrate complexes.[50] The polymer chain, on which the ligand–metal ion complex is located, mimics in this case the protein moiety of an enzyme.

The catalytic influence of polyelectrolytes on the kinetics of simple ligand–metal ion complexation is dependent both on electrostatic and on hydrophobic interactions, as is the case for micellar catalysis.[45] Nevertheless little is known concerning the quantitative part to be attributed to each type of interactions, although the importance of hydrophobic interaction in the catalytic influence of polyelectrolytes has been previously noted by different authors.[51]

We have collected in Table I all the results presently available concerning the influence of polyelectrolytes on some pyridylazo–Ni^{2+} (or –Co^{2+}) complex formation. The observed kinetic constants in the absence of polyelectrolyte (k^0_{obsd}) and in the presence of polyelectrolytes at their largest influence (k_{obsd}) are indicated at 25 °C for the same metal ion and ligand concentrations (respectively 10^{-3} M and 1.25×10^{-5} M). The acceleration or retardation factors are given by the values of the ratios k_{obsd}/k^0_{obsd}. These results show that large acceleration factors (larger than 10) are obtained only with polyelectrolytes bearing hydrophobic groups and moreover only with the more hydrophobic ligands, which is clear evidence of the importance of the hydrophobic interactions between the ligand and the polyelectrolyte. We have also clearly demonstrated that the acceleration observed is a true polyelectrolyte effect, as the replacement of PSS-Na by the same concentration of a model molecule equivalent to a monomeric residue (TS-Na) results in a vanishing of the catalytic effect (Figure 1), which also vanishes when enough salt is added to the polyelectrolyte solutions.[52]

A first important remark concerns the position of the maxima observed in Figure 1: whatever the ligand–Me^{2+} couple considered, the maximum of k_{obsd} occurs for the same polyelectrolyte concentration $C_p \simeq 2.5 \times 10^{-3}$ M. Considering that the binding of Na^+ ions to the polyelectrolyte can be neglected when there are enough divalent ions in the solution to "neutralize" all the charged sites,[53] the fraction of sites occupied by the divalent ions can be estimated from Manning's theory[54] to be $1 - 1/2\xi \simeq 82\%$ in the case of PSS-Na, with ξ being the charge parameter

$$\xi = \frac{e^2}{\epsilon kTb} \qquad (1)$$

(where e is the electronic elementary charge, ϵ is the dielectric constant of the solvent, b is the projection of the distance between two neighboring charges on the polyelectrolyte axis, k is Boltzmann's constant, and T is the absolute temperature). Consequently the concentration of sites occupied at k_{obsd} maxima is $2.5 \times 10^{-3} \times 0.82 \simeq 2 \times 10^{-3}$, that is exactly the equivalent concentration of divalent ions present in the solution, which are thus all bound. It can be concluded from this that the position of the maximum is entirely determined by the electrostatic interactions between the polyelectrolyte and the divalent ions and that it occurs when the free divalent ions are just exhausted.

On the other hand, the amplitude of the maximum strongly depends on the ligand; for example, the ratio k_{obsd}/k^0_{obsd} which is 60.8 for PADA is only 8.05 for PAR which is more hydrophilic when both ligands are mainly in a neutral form. Unfortunately β-PAN, which is more hydrophobic than PADA, can be compared with it only in the presence of dioxane; although a decrease of the acceleration factor from 60.8 to 48.7 is observed for PADA when adding dioxane, this factor is still higher than for β-PAN (27.5). Nevertheless the comparison may be falsified by the fact that one of the results refers to Ni^{2+} and the other to Co^{2+} for the experimental reasons previously indicated. In addition the presence of dioxane may introduce complicating factors such as a shift of the pK of the ligands[55] or preferential solvation changing the local dielectric constant.

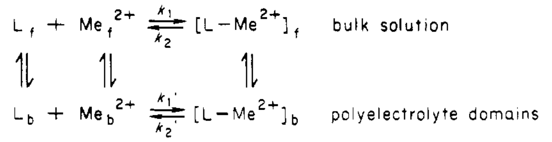
Figure 2 demonstrates the importance of the ionization state of the ligand and the difficulty of working in such conditions that the ligand be uncharged. According to our spectrophotometric determinations, the ionization constant characterizing the equilibrium between PAR and PAR^- does not seem to be affected by the presence of PSS-Na, on the contrary to what happened with PADA[32] (note that PADA can only get a positive charge). The acceleration factor obtained at pH ~5 may be slightly decreased by the contribution of a few percent of the PAR^- form of the ligand. At pH 7, where practically all the ligand is negatively charged, the inhibition observed falls in the very classical case where one species is repelled by the polyion whereas the other one is attracted by electrostatic forces.

The situation is even more complex for the statistical copolymers of STYR-MA for which the charge parameter is not as well-defined as for PSS-Na: (i) it depends on the neutralization degree of the carboxylic functions; (ii) the distance between two consecutive charged sites can only be an average distance due to the statistical distribution of these sites along the polymer chain; (iii) an extended conformation is likely only when the copolymers are fully charged, otherwise a globular conformation stabilized by the hydrophobic interactions between the styrene groups will probably dominate,[56] which renders almost impossible the evaluation of parameter b in eq 1.

The only clear situation in this respect is the one of STYR-MA 32 at pH 8.5, where the copolymer is expected to be fully ionized (this is shown by the titration curve performed in the presence of divalent ions). An average b parameter can be estimated to be on the order of 3.8 Å, which gives a ξ value of 1.87. Neglecting again the presence of monovalent ions, one obtains for the fraction of sites occupied by the divalent ions $1 - 1/2\xi \simeq 0.73$. As the maximum of k_{obsd} occurs for $C_p = 3 \times 10^{-3}$ mol of ionizable groups/L, the concentration of sites occupied is $3 \times 10^{-3} \times 0.73 \simeq 2.2 \times 10^{-3}$, which is again a concentration close to the equivalent concentration of divalent ions present in the solution (an error of 10% is acceptable) and is in agreement with the previous conclusion. Unfortunately it is not possible to perform a similar calculation for the STYR-MA copolymers at pH 7 because they are only partly neutralized; nevertheless the displacement of the maximum of STYR-MA 32 takes place in the expected direction (when the charge parameter is decreased there is a corresponding decrease of the fraction of sites occupied so that more polyelectrolyte is needed to bind all the divalent ions present). The results of Figure 3 also confirm the relation between the amplitude of the catalytic effect and the hydrophobic character of the polyelectrolyte.

Before discussing in more detail the mechanism responsible for the effects observed, we would like to point out the large difference in the acceleration factors determined for two polyelectrolytes having closely related structures: STYR-MA 32 and STYR-MalAc (see Table I). The first one has a catalytic effect more than 7 times larger than the second one although they both have one styrene group per two carboxylic functions. The main structural difference rests on the fact that the $-\mathrm{CO_2}^-$ charged groups are borne by two adjacent carbon atoms of the polymer chain in the case of the maleic acid copolymer, whereas in the other case they are separated by a $-\mathrm{CH_2}-$ link. A strong complexation of Me^{2+} ions, which has been previously discussed,[32,57] is only possible for the maleic acid copolymer. This may result in a retardation effect, analogous to the one observed with polyphosphate,[32,33] competing with the acceleration effect. These remarks show, if still necessary, the large sensitivity of the catalytic effect to specific ion–polyion interactions.

All of the preceding results require a model that will take into account both the "condensation" of divalent ions on the polyelectrolyte and hydrophobic interactions between the polyelectrolyte and the ligand. A kinetic model with comparable requirements has been developed by Diekmann and Frahm[58] in order to interpret the micellar catalysis of a similar ligand (L)–Me^{2+} reaction. Such a model can be made suitable to the present problem. The reaction is assumed to take place both in the bulk solution and in the restricted space of the polyelectrolyte domains according to the following scheme:



where the subscripts f and b refer respectively to free and bound species. (This scheme considers only the 1:1 complex formation discussed here.) The species are also assumed to rapidly exchange between the bulk solution and the polyelectrolyte domains comparatively to the complexation rates (if there was no fast coupling each reaction should be characterized by a different relaxation time). Provided that the condition $[\mathrm{L}] \ll [\mathrm{Me}^{2+}]$ is always fulfilled and assuming $k_1 = k_1'$ and $k_2 = k_2'$,[32,58] the relaxation time can be expressed as

$$1/\tau = k_1\{[\mathrm{Me}^{2+}]_f \times \theta_f + [\mathrm{Me}^{2+}]_b \times \theta_b\} + k_2 \qquad (2)$$

with $[\mathrm{Me}^{2+}]_f$ and $[\mathrm{Me}^{2+}]_b$ being the *effective local concentrations* and

$$\theta_f = [\bar{\mathrm{L}}_f]/([\bar{\mathrm{L}}_f] + [\bar{\mathrm{L}}_b]) \qquad (3a)$$

$$\theta_b = [\bar{\mathrm{L}}_b]/([\bar{\mathrm{L}}_f] + [\bar{\mathrm{L}}_b]) \qquad (3b)$$

the bars indicating equilibrium conditions. These quantities can be expressed in function of the binding constant K characterizing the ligand and polyelectrolyte association

$$\mathrm{L_f} + \mathrm{P} \rightleftarrows \mathrm{L{-}P}$$

and of the polyelectrolyte concentration C_{P} (at least for homopolymers), with P being a monomeric residue

$$K = \frac{[\overline{\mathrm{L{-}P}}]}{[\bar{\mathrm{L}}_f][\bar{\mathrm{P}}]} = \frac{[\bar{\mathrm{L}}_b]}{[\bar{\mathrm{L}}_f](C_{\mathrm{P}} - [\bar{\mathrm{L}}_b])} \simeq \frac{[\bar{\mathrm{L}}_b]}{[\bar{\mathrm{L}}_f]C_{\mathrm{P}}} \qquad (4)$$

the last approximation being true in the experimental conditions where $C_{\mathrm{P}} \gg [\bar{\mathrm{L}}_b]$. It follows that

$$\theta_f = \frac{1}{1 + KC_{\mathrm{P}}} \qquad \theta_b = \frac{KC_{\mathrm{P}}}{1 + KC_{\mathrm{P}}} \qquad (5)$$

The effective local concentrations of Me^{2+} can easily be expressed[32] in function of the charge parameter ξ, the condensation volume v_1, and Avogadro's number N, so that eq 2 can be rearranged in the final form

$$1/\tau = k_1\frac{1000}{1 + KC_{\mathrm{P}}}\left\{\frac{0.5K}{Nv_1}[1 - (2\xi)^{-1}]C_{\mathrm{P}} + \frac{[\mathrm{Me}^{2+}]_{\mathrm{T}} - 0.5[1 - (2\xi)^{-1}]C_{\mathrm{P}}}{1000 - Nv_1C_{\mathrm{P}}}\right\} + k_2 \qquad (6)$$

The equation can only take into account the increasing part of the k_{obsd} variation with C_{P} and becomes meaningless after the maximum catalysis when all the free divalent ions are exhausted. The decreasing part of the curves is to be related to a dilution effect of the reactants in the polyelectrolyte domains when increasing the number of these domains.[2]

For the catalysis of the PADA–Ni^{2+} reaction by PSS-Na[32] or by SDS micelles,[45] the fact that the activation enthalpy at the maximum was almost identical with the activation enthalpy obtained in the absence of polyelectrolyte (55 ± 4 kJ mol^{-1} [44]) was taken as a criterion indicating that the reaction is not catalyzed by lowering the activation energy barrier but only by concentrating the reagents in a small part of the total reaction volume[45] (the activation entropy term is known to be a factor of much less importance than the activation enthalpy term in the water exchange process, which is rate limiting here[45]). These points seemed to justify the assumption that the same rate constants may characterize these reactions as well in the polyelectrolyte or micelle domains as in the bulk ($k_1 = (1.35 \pm 0.15) \times 10^3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_2 = 0.1\ \mathrm{s}^{-1}$ [44]).

This may not be absolutely true for the PADA–Ni^{2+} reaction in the presence of STYR-MA 32 and for the β-

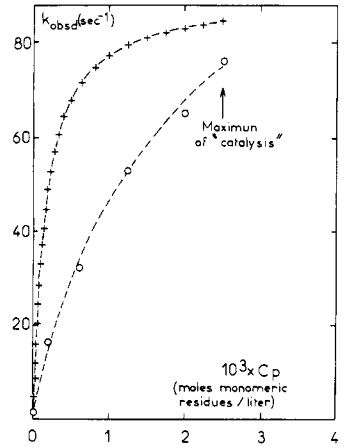


Figure 4. Experimental points for the catalysis of PADA–Ni^{2+} reaction by PSS-Na (O). Theoretical fits with eq 6: $v_1 = 1.02 \times 10^{-20}$ cm^3[32] and $K = 6 \times 10^3$ M^{-1}[54] (–+–); best least-squares fit with v_1 and K as adjustable parameters (see text) (– – –).

PAN–Co^{2+} reaction in the presence of PSS-Na, according to the values of $\Delta H^{\ddagger}$ obtained, which are slightly lower in the presence of polyelectrolyte. The formation of a specific ternary complex between Cu^{2+}, β-PAN, and PSS-Na in H_2O–dioxane has recently been proposed by Yamagishi[50] to explain transient electric dichroism results; a similar situation may exist with Co^{2+}.

Equation 6 contains two generally unknown quantities K and v_1 (K depending on the couple polyelectrolyte–ligand considered and v_1 on the polyelectrolyte–divalent ion couple). An estimation of v_1 has been previously tentatively performed for the PADA–Ni^{2+}–PSS-Na systems by assuming that $\theta_b = 1$ at maximum catalysis[31,32] (v_1 was thus found to be 1.02×10^4 Å^3/monomeric residue). This assumption will be in agreement with the present model provided that the condition $KC_P^{max} \gg 1$ is fulfilled. Now, a binding constant of 6×10^3 M^{-1} has been determined by Kunigi and Ise[59] for the PADA–PSS-Na system at pH 6.9, which would lead to $KC_P^{max} \simeq 15$. A test of the proposed model for the PADA–Ni^{2+}–PSS-Na system using the preceding values shows that although the increase of k_{obsd} is qualitatively predicted, it cannot quantitatively fit the results (see Figure 4). From preliminary dialysis experiments we suspect that the value $K = 6 \times 10^3$ may be largely overestimated, and we have tried to fit the experimental results with eq 6 using a least-squares procedure with two adjustable parameters, v_1 and K. The best fit, which is shown in Figure 4, is obtained with $v_1 = 0.72 \times 10^4$ Å^3 (corresponding to a radius of the cylinder in which counterions are condensed of 30 Å, instead of 36 Å, when the assumption $\theta_b = 1$ at maximum is made) and $K = 0.55 \times 10^3$, which are plausible values. Note that a slight change of the rate constants in comparison to the situation in the absence of polyelectrolyte cannot be completely ruled out (an increase of v_1 could be compensated by an increase of k_1) but is absolutely not required. The model proposed is also susceptible of taking into account a decrease of the maximum amplitude when decreasing K. Experiments are in progress in order to determine independently the K values characteristic of the systems investigated.

In conclusion, the present results have permitted us to characterize more clearly the part played by the hydrophobic interactions in the polyelectrolyte catalysis of simple ligand–divalent metal complex formation. An improved kinetic model is proposed to interpret the results, in which both the condensation of divalent ions on the polyelectrolyte chain by using Manning's theory and the hydrophobic interactions between the ligand and the polyelectrolyte characterized by a binding constant K are taken into account. A quantitative test of the model will be definitely possible when independently determined values of the binding constants K for different ligand–polyelectrolyte couples will be available.

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Registry No. STYR-MA, 9010-92-8; PADA, 13103-75-8; PAR, 1141-59-9; β-PAN, 85-85-8; PSS-Na, 9080-79-9; cobalt, 7440-48-4; nickel, 7440-02-0.

References and Notes

(1) Morawetz, H. *Acc. Chem. Res.* **1970**, *3*, 354.
(2) Morawetz, H.; Vogel, B. *J. Am. Chem. Soc.* **1969**, *91*, 563.
(3) Morawetz, H.; Gordimer, G. *J. Am. Chem. Soc.* **1970**, *92*, 7532.
(4) Cho, J. R.; Morawetz, H. *J. Am. Chem. Soc.* **1972**, *94*, 375.
(5) Okubo, T.; Ise, N. *Proc. R. Soc. London, Ser. A* **1972**, *327*, 413.
(6) Ise, N.; Okubo, T. *Nature (London)* **1973**, *242*, 605.
(7) Ise, N.; Matsuda, Y. *J. Chem. Soc. Faraday Trans. 1* **1973**, *69*, 99.
(8) Okubo, T.; Ise, N. *J. Am. Chem. Soc.* **1973**, *95*, 2293.
(9) Mita, K.; Kuniki, S.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 936.
(10) Kunugi, S.; Okubo, T.; Ise, N. *J. Am. Chem. Soc.* **1976**, *98*, 2282.
(11) Mita, K.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1033.
(12) Ise, N. *J. Polym. Sci., Polym. Symp.* **1978**, *62*, 205.
(13) Ise, N.; Okubo, T. *Macromolecules* **1978**, *11*, 439.
(14) Enokida, A.; Okubo, T.; Ise, N. *Macromolecules* **1980**, *13*, 49.
(15) Ishiwatari, T.; Okubo, T.; Ise, N. *Macromolecules* **1980**, *13*, 53; *J. Polym. Sci., Poly. Chem. Ed.* **1980**, *18*, 1807, 1815.
(16) Ise, N.; Maruno, T.; Okubo, T. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 485.
(17) Okubo, T.; Maruno, T.; Ise, N. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 501.
(18) Maruno, T.; Okubo, T.; Ise, N. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 667.
(19) Sugimura, M.; Okubo, T.; Ise, N. *Macromolecules* **1981**, *14*, 124.
(20) Ishiwatari, T.; Maruno, T.; Okubo, M.; Okubo, T.; Ise, N. *J. Phys. Chem.* **1981**, *85*, 47.
(21) Ise, N. *Makromol. Chem. Suppl.* **1981**, *5*, 107.
(22) Ise, N.; Okubo, T.; Kunugi, S. *Acc. Chem. Res.* **1982**, *15*, 171.
(23) Ise, N.; Okubo, T.; Yamamura, Y. *J. Phys. Chem.* **1982**, *86*, 1694.
(24) Fernandez-Prini, R.; Turyn, D. *J. Chem. Soc., Faraday Trans. 1* **1973** *69*, 1326.
(25) Turyn, D.; Baumgartner, E.; Fernandez-Prini, R. *Biophys. Chem.* **1974**, *2*, 269.
(26) Fernandez-Prini, R.; Baumgartner, E. *J. Am. Chem. Soc.* **1974**, *96*, 4489.
(27) Baumgartner, E.; Fernandez-Prini, R. In "Polyelectrolyte"; Frisch, K. C., Lemper, D., Patsis, A., Eds.; Technomic: 1976.
(28) Fernandez-Prini, R.; Baumgartner, E.; Turyn, D. *J. Chem. Soc.* **1978**, *74*, 1196.
(29) Fernandez-Prini, R. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2460.
(30) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.
(31) Tondre, C. *C. R. Hebd. Seances Acad. Sci., Ser. II* **1981**, *292*, 713.
(32) Tondre, C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1795.
(33) Sbiti, N.; Tondre, C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1809.
(34) De Maria, P.; Fini, A.; Ferruti, P.; Beni, M. C.; Barbucci, R. *Macromolecules* **1982**, *15*, 679.
(35) Meisel, D.; Rabani, J.; Meyerstein, D.; Matheson, M. S. *J. Phys. Chem.* **1978**, *82*, 985.
(36) Meyerstein, D.; Rabani, J.; Matheson, M. S.; Meisel, D. *J. Phys. Chem.* **1978**, *82*, 1879.
(37) Sassoon, R. E.; Rabani, J. *Isr. J. Chem.* **1982**, *22*, 138.
(38) Tondre, C.; Zana, R. *J. Phys. Chem.* **1972**, *76*, 3451.
(39) Nikolayev, A. F.; Gal'Perin, V. *Vysokomol. Soedin., Ser. A* **1967**, *A9*, 2469; *Polym. Sci. USSR (Engl. Transl.)* **1967**, *9*, 2793.
(40) Mochizuki, K.; Imamura, T.; Ito, T.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1743; *Chem. Lett.* **1977**, 1239.

Macromolecules **1984**, *17*, 375–380

(41) Holyer, R. H.; Hubbard, C. D.; Kettle, S. F.; Wilkins, R. G. *Inorg. Chem.* **1966**, *5*, 622.

(42) Hubbard, C. D.; Pacheco, D. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1373.

(43) Cobb, M. A.; Hague, D. N. *Trans. Faraday Soc.* **1971**, *67*, 3069.

(44) Cobb, M. A.; Hague, D. N. *J. Chem. Soc. Faraday Trans. 1* **1972**, *68*, 932.

(45) James, A. D.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 10.

(46) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 97. Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *No. 49*, 55.

(47) p*K* values for the protonation of the ring nitrogen and for ionization of the hydroxyl group are respectively 2.32 and 12.0 in 50/50 water–methanol (ref 48) and 2.0 and 12.3 in 50/50 water–dioxane (ref 42).

(48) Anderson, R. G.; Nickless, G. *Analyst (London)* **1968**, *93*, 13.

(49) Hnilickova, M.; Sommer, L. *Collect. Czech. Chem. Commun.* **1961**, *26*, 2189.

(50) Yamagishi, A. *J. Phys. Chem.* **1981**, *85*, 2665.

(51) See for instance: Ise, N. In "Charged and Reactive Polymers"; Rembaum, A., Selegny, E., Eds.; D. Reidel: Dordrecht, Holland, 1975; Vol. 2 and references therein.

(52) Tondre, C.; Sbiti, N. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23*, 67.

(53) Manning, G. S. In "Charged and Reactive Polymers"; Selegny, E., Ed.; D. Reidel: Dordrecht, Holland, 1974; Vol. 1, p 14.

(54) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.

(55) Baumgartner, E.; Fernandez-Prini, R.; Turyn, D. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1518.

(56) Conio, G.; Patrone, E.; Russo, S.; Trefiletti, V. *Makromol. Chem.* **1976**, *177*, 49.

(57) Tondre, C.; Zana, R. *J. Phys. Chem.* **1971**, *75*, 3367.

(58) Diekmann, S.; Frahm, J. *J. Chem.* Soc., *Faraday Trans. 1* **1979**, *75*, 2199.

(59) Kunugi, S.; Ise, N. *Z. Phys. Chem. (Frankfurt/Main)* **1974**, *92*, 69.

Ellipsometry Studies of Adsorbed Polymer Chains Subjected to Flow

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ABSTRACT: Ellipsometry has been applied to study the average thickness of adsorbed polymer layers under flowing conditions. The measurement also produces a simultaneous determination of the surface concentration. Measurements have been conducted under flowing pure solvent at the Θ-temperature on four polystyrene samples of molecular weights ranging from 1.8×10^6 to 20×10^6 adsorbed previously onto chrome from quiescent cyclohexane solutions. No detectable changes in film thickness were observed for the three lower molecular weight samples over the whole range of velocity gradients applied. On the other hand, the film thickness of the 20 million molecular weight sample began to decrease as the apparent velocity gradient surpassed 2000 s^{-1} and decreased as much as 15% when the apparent velocity gradient reached 7800 s^{-1}. The response of the adsorbed polymer layer to the imposition of the flow over short periods of time was reversible, and no change in adsorbance was observed between the inception and cessation of the flow. The measured conformational changes were also compared to the predictions of a simple bead-and-spring model of an attached polymer segment, and qualitative agreement was obtained when the effect of finite extensibility was included in the model.

Introduction

Polymer adsorption has been the focus of considerable attention in recent years because of a large number of processes in which this phenomenon is important. The majority of work, however, has been devoted to the case of adsorbed chains in quiescent systems, and relatively few studies have considered the effect of hydrodynamic forces on the adsorbed layer. Since most applications in which polymer adsorption is important involve the presence of a flow field (enhanced oil recovery, lubrication, liquid chromatography, and filtration), there is a need for understanding the interactions of the dangling ends and loose loops making up the adsorbed layer of polymer chains and hydrodynamic forces arising from the flow of liquid above the solid–liquid interface.

Hydrodynamic forces can affect the adsorbed layer in one of two ways. The first case is one in which the polymer chains are first adsorbed under no-flow conditions and then subjected to the flow of the bulk liquid above the surface. For a weakly adsorbed, high molecular weight, flexible chain (the case often encountered in industrial applications), only a small proportion of the polymer segments is actually attached to the surface with the remainder extending away from the surface as dangling ends or loose loops. The imposition of hydrodynamic forces can result in distortion and alignment of those unattached segments. Furthermore, if the shear stress is large enough, it is conceivable that the chains could be torn away from the surface.

The second case where the importance of flow should be investigated is one where the chains are adsorbed from a flowing solution. This could result in flow-induced deformation and orientation of the polymer chains prior to attachment to the surface. It is possible that such changes in conformation could affect both the kinetics of the adsorption and the final conformation of the film. This paper is strictly concerned with the first case, where the polymer is adsorbed from quiescent solutions. The second case will be the subject of a later paper.

The previous studies in this area which most convincingly demonstrate the possibility of flow-induced changes in the conformation of polymer films are those reported by Gramain and Myard[1] and, more recently, by Cohen and Metzner.[2] In both studies, a simple hydrodynamic method was used to infer the properties of polymer films in the presence of flow. This is carried out by measuring the pressure drop required to sustain a given flow rate through either a porous media[1] or a capillary tube.[2] From such measurements, the effective hydrodynamic thickness of an adsorbed layer can be estimated if it is assumed that the increased hydrodynamic resistance due to the film comes about solely from a constriction of the path through which the fluid is flowing by the adsorbed polymer layer. The study of Gramain and Myard[1] utilized the flow of pure

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