

## Adsorbed Polymers in Colloidal Systems: from Statics to Dynamics

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**ABSTRACT:** When (homo-) polymers adsorb from solution onto a surface, forming reversible, physical bonds with the surface, a diffuse structure results which can be characterized in several ways. On the level of individual molecules one may distinguish between sequences of monomer units attached to the surface ('trains'), parts which start from the surface and return there ('loops') and parts where one end dangles freely in solution ('tails'). On the level of the adsorbed layer as a whole one is interested in the density of monomer units as a function of distance from the surface (the so-called profile), the (total) adsorbed mass, and the thickness of the layer. Of course all these properties depend on the molar mass of the polymer, its structure and its interaction with the surface and with the solvent.

The static (equilibrium) situation has been studied in depth over the past 20 years, both experimentally and theoretically. A particularly important step forwards was the theoretical work of Scheutjens et al. who developed an elegant and exact method to calculate adsorbed polymer properties on the basis of a lattice model. Together with results from modern experimental techniques (e.g., small angle neutron scattering, photo-correlation spectroscopy) a fairly consistent picture is now established and work is directed towards more complicated systems such as copolymers and polyelectrolytes.

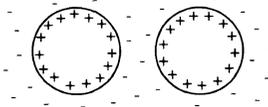
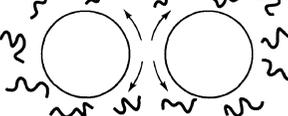
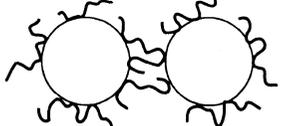
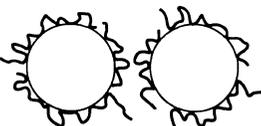
The kinetics of the adsorption process however, is much less understood and the same holds for the dynamics of adsorbed chains. Although it was long suspected that slow rearrangement processes occur in adsorbed layers, it was shown only recently that a freshly prepared polymer layer thins in the course of time as long as the surface is unsaturated.

This has important consequences for the process of flocculation (aggregation) of colloidal particles by adsorbed polymer. Such aggregation will namely occur only if the polymer molecules can bridge the gap between two particles in close proximity (so-called 'bridging' flocculation). If the particles repel each other (e.g., by virtue of their electrical charge) they may not approach closely enough for bridging to occur. Big polymer molecules can however bridge a gap of 100 Å or more, provided they have not yet had time to rearrange into a flat conformation. Hence, only if adsorption occurs rapidly enough to compete successfully with the rearrangement process, there is the possibility of floc formation.

Recent attempts to get more direct information on the kinetics of adsorption, desorption and exchange will be reviewed.

**KEY WORDS:** Polymer Adsorption / Kinetics / Bridging Flocculation / Layer thickness / Exchange / Conformations / FTIR / Streaming Potential / Reflectometry

An interesting way to influence the interactions between dispersed colloidal particles is to surround them with a soluble, flexible polymer.<sup>1,2</sup> Several things may then happen. Firstly the polymer may stay in solution. this might seem to be a trivial case but it is not: the fact that swollen polymer coils are expelled from the surface of the particle (the depletion effect) creates a subtle osmotic attraction between the particles, which can lead to aggregation.<sup>1, 3, 4</sup> Secondly, the polymer may adsorb to the surface of the particles. It then may happen that some chains adsorb on two (or more) different particles, thereby pulling them together.<sup>2, 5, 6</sup> This is usually called 'bridging'. Alternatively, the polymer may build up a protective sheath around individual particles, thereby preventing them from sticking together. The term for this effect is steric stabilization. We note in passing that particles in aqueous dispersions without added polymer are usually stabilized by electrostatic forces. Figure 1 summarizes the various kinds of interaction.

MECHANISM	FORCE LAW
<p>(A) bare particles</p> 	<p><u>Van der Waals attraction</u></p> <p><u>electrostatic repulsion</u></p>
<p>(B) particles + non-adsorbing polymer</p> 	<p>weak (osmotic) attraction</p> <p><u>"depletion attraction"</u></p>
<p>(C) particles + low polymer dose adsorbed</p> 	<p>strong attraction</p> <p><u>"bridging"</u></p>
<p>(D) particles + excess adsorbing polymer</p> 	<p>strong repulsion</p> <p><u>"steric repulsion"</u></p>

**Figure 1.** Schematic overview over various forces between colloidal particles with and without polymer.

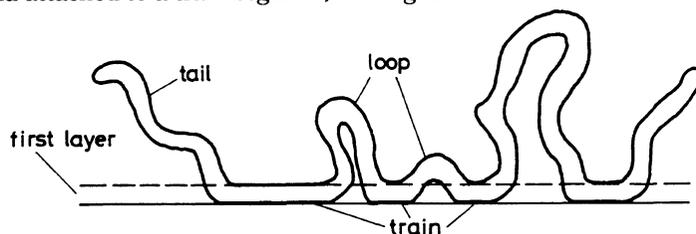
Most synthetic polymers are flexible objects which can assume different shapes in different environments. Also, since changes in these shapes must always be realized under the constraint that the chains do not break, topological constraints play an important role and polymers have typically, very slow dynamics.<sup>7</sup> For these two reasons, colloidal dispersions with polymers display complicated behaviour, and understanding these systems is far from complete. In the following, we shall focus our attention to the adsorption of polymers and to the bridging phenomenon. We will first neglect time effects and review what is known about the statics of adsorbed polymers. In particular, we shall discuss the thickness of adsorbed layers, since this quantity determines at what distance two particles with adsorbed polymer start to interact. We shall then discuss the origin of the bridging attraction and present some experimental data on the kinetics of bridging flocculation. This will bring us to the conclusion that

more insight is needed into the dynamics of the adsorption process and attempts to study this shall be reviewed.

#### Polymer adsorption: statics

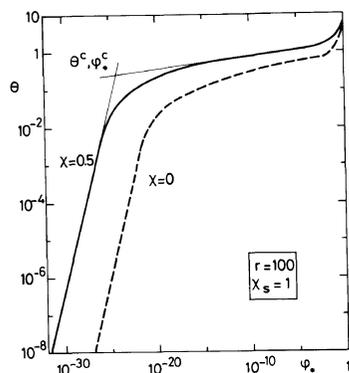
Many early studies of polymer adsorption were entirely empirical; theoretical understanding developed slowly.<sup>8, 9</sup> Some interesting theoretical approaches were published between 1966 and 1974,<sup>10-12</sup> but much insight was gained when Scheutjens and Fleer presented their now classical theory.<sup>13, 14</sup> This theory is capable, albeit by numerical computation, to deal with relevant chain lengths (from monomers to long polymers) and densities without making other approximations than a lattice description of the solution adjacent to the adsorbing wall. Another great advantage is that the formalism can easily be extended to polydisperse polymers and mixtures, (block-) copolymers, terminally anchored polymers, association phenomena (micellization), lipid bilayers, adsorbed polyelectrolytes etc.<sup>15-19</sup>

The predictions of the theory for physically adsorbed, simple homopolymers have been discussed in detail elsewhere;<sup>14, 15</sup> we recall here the main laws. The conformations of adsorbed chain molecules are most easily described in terms of trains (sequences of monomer units all in contact with the substrate) and loops (sequences bounded by trains at both ends, and protruding in the solution) and tails (sequences with only one end attached to a train segment). See fig. 2.



**Figure 2.** Pictorial representation of an adsorbed polymer showing trains, loops and tails.

The monomer density falls monotonously with distance from the surface (this function is called the segment density profile). Going outward from the substrate one first has the train layer which is densest, then follows a zone dominated by loops and, finally, a very dilute periphery where mostly tails occur. In some cases, it is possible to determine segment density profiles by means of small angle neutron scattering.<sup>15, 20</sup>



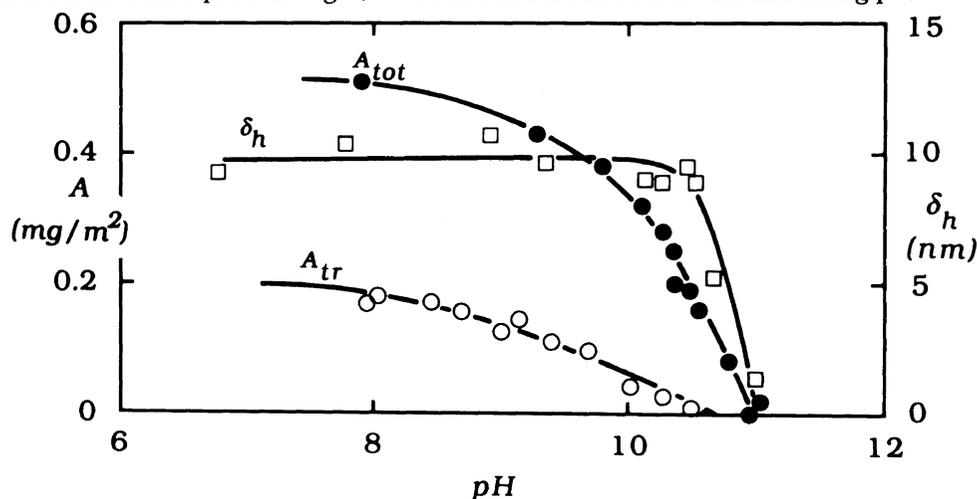
**Figure 3.** Typical polymer adsorption isotherms over a wide range of concentrations for chains of 100 segments from a thermal and a  $\Theta$  solvent, plotted double-logarithmically. The initial steep rise (where essentially isolated chains populate the surface) and the plateau region (where adsorbed chains interact strongly) meet in the point  $\theta_c, \phi_c$ .

Adsorption isotherms for not too weak adsorption have a characteristic shape (see fig. 3).<sup>21</sup> Adsorption increases rapidly at extremely low concentrations; in practice, no equilibrium concentration can be detected in this region. Such behaviour is usually referred to as 'high affinity' adsorption. Then, the adsorption suddenly saturates at a more or less well-defined value, called the 'plateau'. Along the isotherm, the average conformations of the adsorbed chains are very different for the two regions: in the 'high affinity' part, very flat conformations are found with small loops and almost no tails. When the plateau region is approached, loops and long tails appear, and the thickness of the layer grows rapidly.

At fixed equilibrium concentration, similar changes (albeit more gradual) are found when the chain length is increased. Loops and tails increase in size and as a consequence, the adsorbed mass  $A$  goes up. This happens in a way which is characteristic for the solvency of the polymers: in good solvents, the coverage reaches a plateau at very high molecular weight, whereas in  $\Theta$ -solvents, it appears to increase as  $\log M$ , i.e. without bounds.<sup>21</sup> Experiments with polystyrene adsorbing onto silica from cyclohexane<sup>22</sup> and with polyethylene oxide on silica from water<sup>23</sup> provide excellent illustrations of each of these respective cases.

Early experimental work was devoted to measuring the adsorbed amount, but experiments revealing loops, trains and tails proved much harder. A particularly useful and recent way to distinguish trains from other chain parts is by making use of the fact that solvent bound to train segments has a considerably reduced mobility. This shows up as an enhanced proton magnetic relaxation rate of the solvent;<sup>24</sup> loops and tails do not contribute to the effect. We shall discuss one example below.

Loops and tails cannot be distinguished from each other. However, there is rather compelling indirect evidence of the existence of tails in hydrodynamic experiments. Tails, although too dilute to show up in, e.g., neutron scattering, are very effective in impeding tangential solvent flow.<sup>25</sup> Therefore, they determine to a large extent the so-called hydrodynamic layer thickness  $\delta_H$ , i.e. the thickness one measures by monitoring changes in hydrodynamic radius of a particle or capillary. As is often the case, a combination of several techniques is very helpful in understanding the structure of the polymer layer. One instructive example is presented in fig. 4 where three measured quantities (total adsorbed amount, amount of trains and  $\delta_H$ ) are given as a function of the effective adsorption strength, which in this case decreases with increasing pH.



**Figure 4.** Adsorption-desorption transition for PEO on silica in  $\text{H}_2\text{O}$  of varying pH, as seen by total adsorbed amount  $A$ , amount of trains  $A_{tr}$  and hydrodynamic layer thickness  $\delta_H$ .

At the transition from adsorption to desorption (arrow) all three quantities have become zero. However, the decay of  $A_{tr}$  is most gradual and extends over  $\sim 5$  pH units,

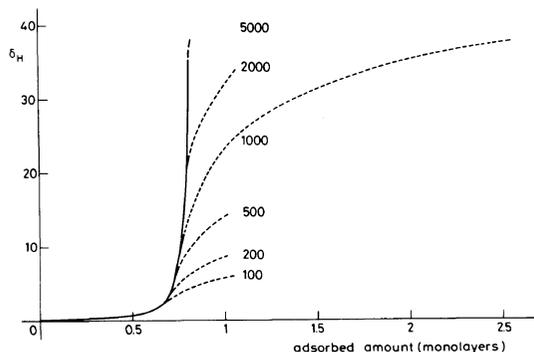
whereas that of  $\delta_H$  occurs in a narrow pH range and is therefore very steep; the total adsorbed amount  $A$  displays intermediate behaviour. Hence, as one approaches the transition, the train density first decreases and the total coverage follows this more slowly, but  $\delta_H$  (i.e. the extension of the tails) is not affected. Very close to the desorption transition we find situations where the train density and adsorbed amount are already nearly zero, but the thickness is still at its plateau value. This means that we are dealing with a few swollen and loosely attached coils, a situation which can only exist when the effective adsorption energy per segment is well below  $kT$ .

#### A closer look at layer thickness

We noted already that the thickness of the adsorbed layer is an important quantity in the context of interaction between colloidal particles. Also, we saw that layer thickness is mainly determined by long tails protruding into the solution and that these tails appear when the adsorbed layer becomes saturated, i.e. at finite equilibrium concentration. One can calculate hydrodynamic layer thicknesses from theoretical segment density profiles, by treating these as layers with a permeability which varies with distance from the substrate (porous layer model). The relevant equation (Debye-Brinkman equation) reads:

$$\eta_0 \left( \frac{d^2 v}{dz^2} - \frac{v}{k(z)^2} \right) = -\text{grad } P \quad (1)$$

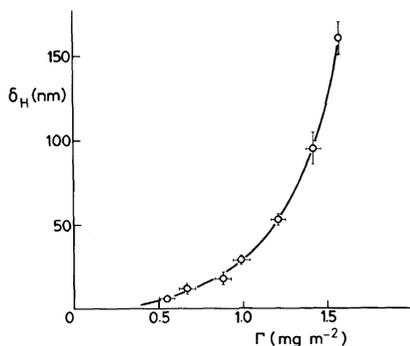
where  $v(z)$  is the solvent velocity profile along direction  $z$  normal to the surface,  $\eta_0$  is the solvent viscosity,  $P$  is the pressure and  $k(z)$  is a permeability taking into account that the porosity of the polymer layer increases with increasing  $z$ . When the calculation is carried out, it turns out that indeed the tails determine the thickness almost entirely.<sup>26</sup> Another interesting result is the relation between  $\delta_H$  and  $A$ , see fig. 5



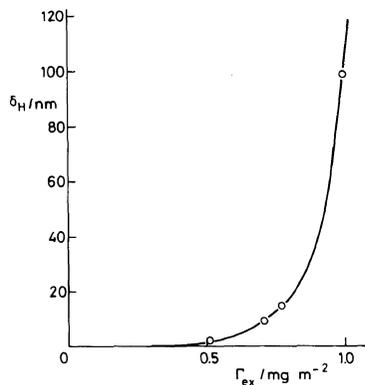
**Figure 5.**  $\delta_H$  as a function of adsorbed amount for various chain lengths. The curves coincide at low bulk concentration (full curve) but diverge as the bulk concentration increases (dotted curves).

Figure 5 shows curves for 6 different chain lengths. Surprisingly, all results at relatively low bulk concentrations can be represented by one single curve. This implies that not the molecular weight but the adsorbed amount (indicated by  $\Gamma$  in fig. 5) is the key variable. Of course, the adsorbed amount itself is a function of molecular weight (and concentration), but as soon as  $\Gamma$  is fixed, this determines  $\delta_H$  completely (unless the concentration becomes too high, dotted curves). Another important feature to note is the steep increase at high  $\Gamma$ : this is the region where we have saturated layers so that rather long tails can develop. It should be emphasized that for good solvents the increase may be so steep that very small (in fact undetectable) changes in  $\Gamma$  may still produce substantial changes in  $\delta_H$ . In the unsaturated, low  $\Gamma$ , part of the curve  $\delta_H$  is low and varies only a little: adsorbed chains adopt very flat conformations, i.e. shapes very different from those of coils in solution. Dynamic light scattering experiments on

polymer-coated colloidal particles have confirmed these predictions very convincingly, as is clear from fig. 6.<sup>26</sup> With this method, the layer thickness is obtained from a change in the diffusion coefficient of particles when they get covered by polymer.<sup>15</sup> An alternative method (which can be used when the surface is charged but the polymer is neutral) is to determine the  $\zeta$ -potential before and after polymer adsorption. From the ratio of these, a hydrodynamic thickness can also be obtained, provided the salt concentration is sufficiently low.<sup>27</sup>



**Figure 6.** Hydrodynamic layer thickness  $\delta_H$  as a function of adsorbed amount  $\Gamma$  for polyethylene oxide adsorbed from water on PS latex.<sup>26</sup>



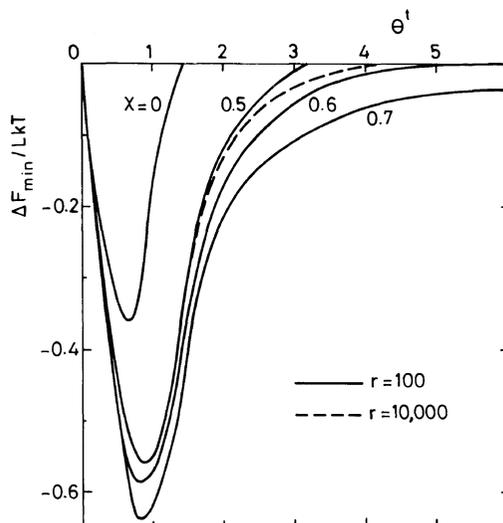
**Figure 7.** Hydrodynamic layer thickness  $\delta_H$  as a function of adsorbed amount  $\Gamma$  for polyvinylpyrrolidone adsorbed from water on glass.<sup>29</sup>

Both electrophoresis<sup>28</sup> and streaming potential<sup>29</sup> have been used to obtain  $\zeta$ . Streaming potential measurements offer some advantages to which we return below. In fig. 7 we show one more  $\delta_H$  versus  $\Gamma$  plot, this time obtained from streaming potential measurements. Again, we see a rather flat initial part at low  $\Gamma$  and a very steep increase when the layer gets saturated.

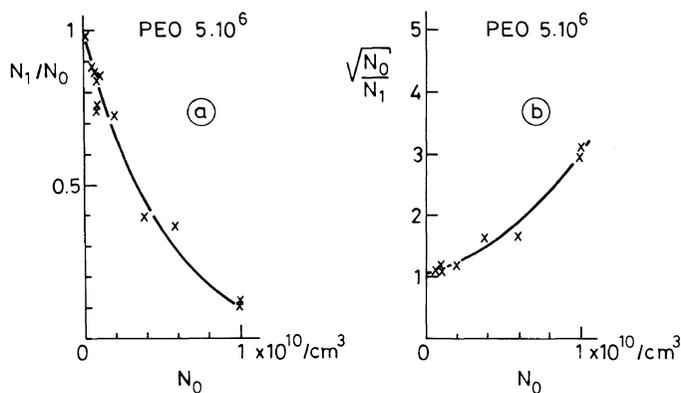
#### Bridging flocculation: Statics

Scheutjens and Fleer have not only used their theory for the study of adsorption onto one surface, but also to investigate the interaction between two surfaces with adsorbing polymer between them.<sup>30</sup> By varying the distance between the two (parallel) surfaces and calculating the excess free energy for each distance, one obtains interaction curves. The relevant case is that of 'restricted equilibrium', i.e. a fixed amount of polymer between the plates (indicated by  $\Theta^l$  in fig. 8), while the solvent can escape but has a fixed chemical potential; of course conformations are allowed to equilibrate fully. It turns out from these calculations that fully covered, saturated layers tend to repel at all distances, but that unsaturated ('starved') layers can form bridges and as a result display an attractive minimum. The depth of this minimum depends on the amount of polymer  $\Theta^l$  between the two surfaces as can be seen in fig. 8.

Clearly, it is not necessary for attraction to occur, that the solvent is poor ( $\chi \geq 0.5$ ); bridging attraction is also possible in good solvents. However, in very poor solvents there is always an attractive minimum, even for very high coverage, whereas saturated polymer layers in good solvents are only repulsive. The results of fig. 8 correspond nicely to the observation that fully covered colloidal particles are usually very stable against aggregation,<sup>1</sup> whereas optimum aggregation occurs at a polymer dose corresponding to roughly half the plateau coverage. By way of example, we present in fig. 9 an experimental result for polystyrene latex particles flocculated by polyethylene oxide. When the number of remaining singlet particles (which is a measure of the extent of aggregation) is plotted as a function of the amount of polymer added, a clear stability minimum is observed.<sup>31</sup>



**Figure 8.** Free energy minimum due to bridging as a function of the total amount of polymer  $\Theta^t$  between two plates. Solid curves refer to short chains (100 segments); dashed curve is for  $10^4$  segments. Different curves refer to different solvencies; the value of the Flory-Huggins  $\chi$ -parameter is indicated.



**Figure 9.** Flocculation of polystyrene latex by polyethylene oxide: the effect of polymer dose on the fraction of singlets  $N_1/N_0$  remaining.

(a) molecular weight  $3 \cdot 10^6$ , initial particle concentration  $N_0 = 3 \cdot 10^{16} \text{ m}^{-3}$ . x no salt added;  $[\text{KNO}_3] = 10^{-2} \text{ mol dm}^{-3}$ .

(b) molecular weight  $7.7 \cdot 10^6$ ,  $N_0 = 2.6 \cdot 10^{16} \text{ m}^{-3}$ , no salt added.

#### Bridging Flocculation: Kinetics

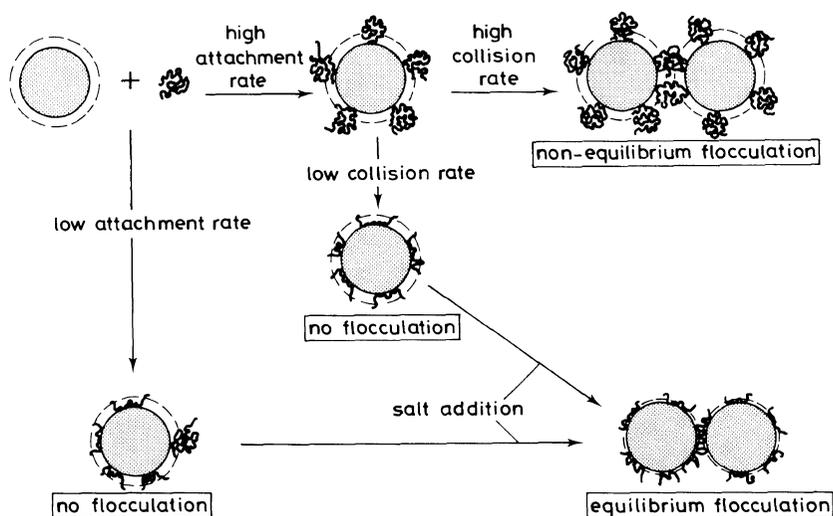
Given the fair agreement between theory and experiment concerning the statics of the bridging interaction, it was tempting to study the flocculation process in more detail. This was done recently by Pelssers<sup>31</sup> who investigated how the size distribution in a flocculating latex evolved with time. Before discussing some of his results, we recall that the classical theory of flocculation due to Von Smoluchowski<sup>32, 33</sup> predicts a gradual decrease in the number of singlets  $N_1$  with time  $t$ , and also, at fixed time, with the initial singlet concentration  $N_0$ :

$$N_1(t) = N_0 (1 + k_f N_0 t)^{-2} \quad (2)$$

where  $k_f$  is a flocculation rate constant, which depends, among other things, on the interaction potential between the particles. If this interaction is time invariant,  $k_f$  is constant during the flocculation process.

Pelssers' results were completely at variance with Eq. 2, indicating that flocculation was initially rapid (high  $k_f$ ) but then stopped entirely, despite the fact that a large number of singlets was still present ( $k_f$  zero). The final reduction in singlet concentration (at fixed polymer coverage) turned out to depend on the initial particle concentration in a very peculiar way.

We realized that these results were due to a loss of 'reactivity' of the particles and we attributed this loss to the fact that freshly adsorbed polymer molecules first extend far enough from the particle surface to bridge the interparticle distance during an encounter, but that after some time the chains would lie flat on the 'starved' surface, thereby losing their capability to form bridges. Figure 10 summarizes the possible scenarios.



**Figure 10.** Schematical representation of the mechanisms of bridging flocculation in dispersions of charged particles.

Bridging flocculation at low salt concentration occurs as long as a sufficient number of extended ('active') adsorbed chains per particle are present. This means that the attachment process by which the particles acquire adsorbed polymer must compete with the reformation process and that the relative rates of these two determine whether particles can flocculate by bridging or not. A simple kinetic model was developed which could quantitatively account for the data.<sup>34</sup> For the polystyrene latex/polyethylene oxide system, one finds a reformation time of 3.4 seconds.

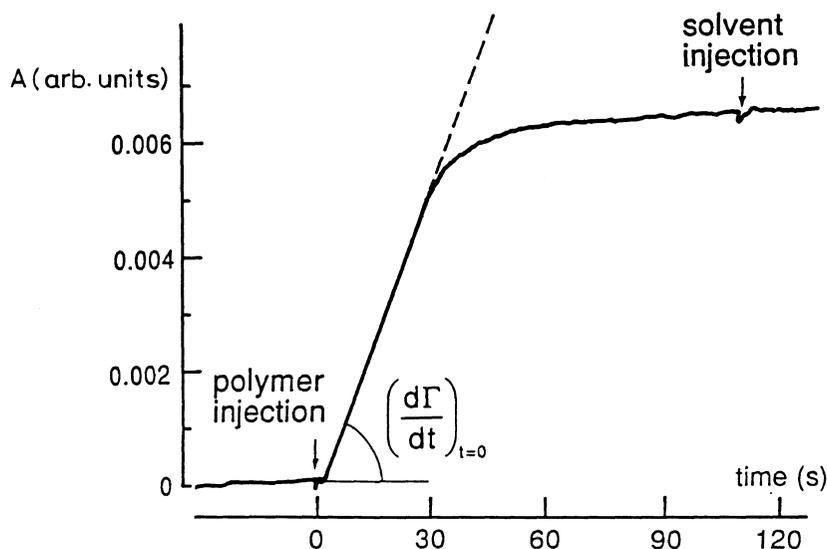
The observations discussed above indicated that it is not only the thermodynamic equilibrium, but certainly also the dynamics which determines whether or not the dispersion will aggregate, and how rapidly this will occur. The kinetics and dynamics of polymer adsorption is a rather new field of study. Let us now discuss a few recent experimental approaches.

#### Adsorption Kinetics: Experimental Attempts

Any adsorption process has at least two steps: (1) transport towards the surface (usually by diffusion or convection) and (2) attachment (the rate of which may generally depend on some potential barrier, which may include a repulsion by preadsorbed

molecules). In addition to this, flexible polymers have to undergo a reformation process after attachment and it is conceivable that this latter process has an important influence on the overall rate.

Obviously, the overall rate is an important piece of information. However, there are not many ways to determine this rate with sufficient accuracy and under proper control of the bulk mass transfer process. We used a reflectometer to follow polymer deposition from a controlled 'impinging jet' flow.<sup>23</sup> Figure 11 shows an example of adsorption versus time as measured for PEO adsorbing on SiO<sub>2</sub> from water. This result has a number of interesting features.



**Figure 11.** Example of a typical experiment for PEO adsorption on SiO<sub>2</sub> from 'impinging jet' flow.  $M = 4 \cdot 10^5$  g/mole,  $c = 10$  mg dm<sup>-3</sup>,  $Re = 12.2$ .

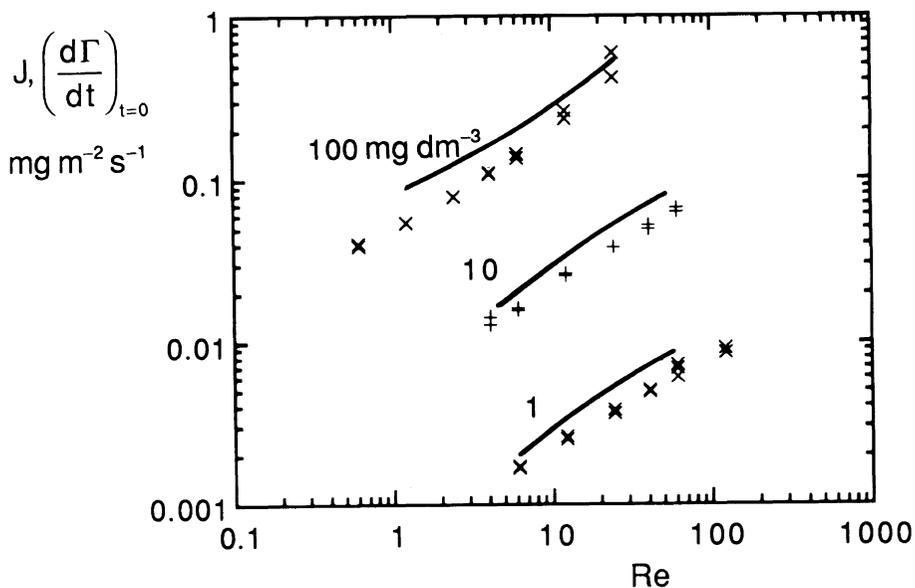
Firstly, up to 80% or more of the maximum coverage, the adsorption rate is constant, and one can check in detail that this rate equals the bulk mass transfer rate,  $J$ , given by

$$J = 0.776 \nu^{1/3} R^{-1} D^{2/3} (\bar{\alpha} Re)^{1/3} c \quad (3)$$

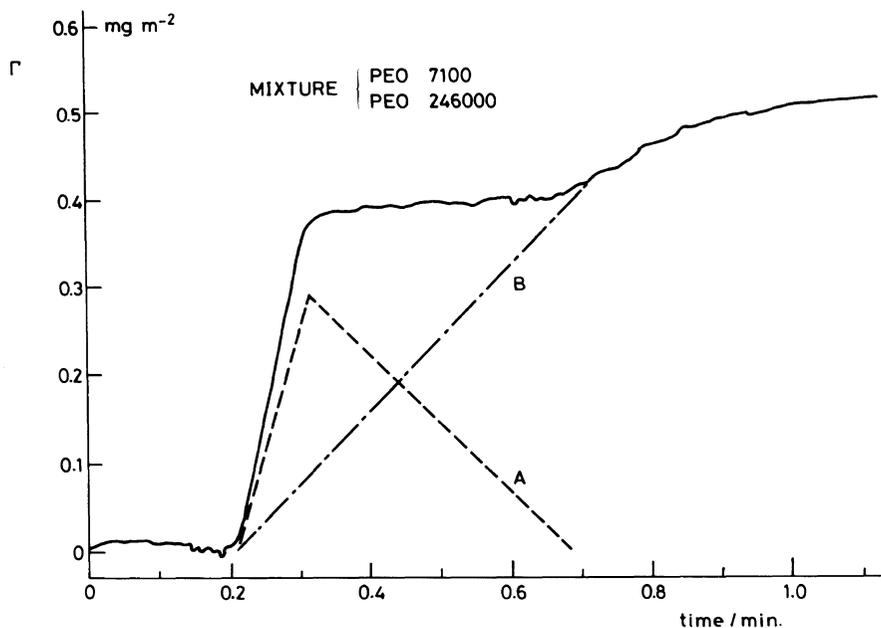
where  $\nu$  is the kinematic viscosity of the solvent,  $R$  the radius of the tube from which the impinging jet emerges,  $D$  the diffusion coefficient,  $\bar{\alpha}$  a function of the flow rate,  $Re$  the Reynolds' number and  $c$  the concentration. In fig. 12 we compare initial adsorption rates with  $J_0$ .

This result means that for the PEO/SiO<sub>2</sub>/H<sub>2</sub>O system, there is no rate-determining attachment step up to rather high coverage, even at the highest  $J$  that we could attain.

Secondly, when  $\Gamma$  approaches saturation, the adsorption drops quite suddenly to zero. Current models of adsorption usually assume a linear dependence on the degree of saturation:  $1 - \Gamma/\Gamma_{\max}$ <sup>35</sup>, but this is clearly inconsistent with our data. Anyhow, the attachment step is only rate-determining over a small range of coverage, and its rate changes very rapidly with increasing coverage. Thirdly, desorption could possibly occur after exchanging the equilibrium solution with pure solvent (see arrow in fig. 11). However, if this is done, no desorption is detectable for this molecular weight ( $4 \cdot 10^5$  g/mole) within the (very good) resolution of the experiment; it is certainly less than 2%.



**Figure 12.** Initial adsorption rates  $\frac{d\Gamma}{dt}$  (crosses) and bulk mass transfer rates  $J$  (solid curves) as a function of Reynolds' number ( $Re$ ) for three different concentrations of PEO ( $M = 246,000$  g/mole) adsorbing from water onto  $SiO_2$  from an 'impinging jet' flow.

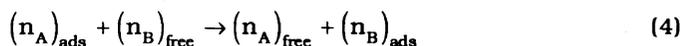


**Figure 13.** Adsorption kinetics of a mixture of two monodisperse PEO samples A and B.  $M_A = 7100$  g/mole,  $M_B = 246,000$  g/mole.

With lower molecular weights some desorption was observed (up to 15% for  $M = 7100$  g/mole), but even for these cases it was extremely slow.

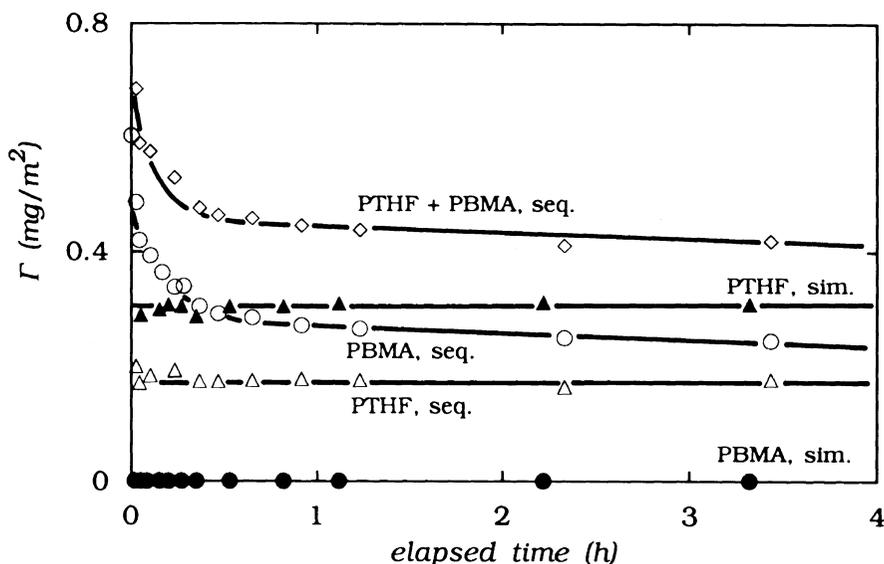
An interesting result is obtained when a mixture of two PEO samples A and B ( $M_A = 7100$  g/mole and  $M_B = 246000$  g/mole) is used. The kinetic curve for that case is shown in fig. 13.

Now the maximum coverage is reached in two steps. First, the surface is largely covered with the smaller molecules (with the larger diffusion rate), after which  $\Gamma$  stays constant for a while. However, the surface populations of A and B cannot remain constant since B must displace A because of its larger molecular weight. Apparently, this exchange occurs on an equal mass basis:



with  $n_A/n_B = M_B/M_A$ . Also, the exchange can fully keep up with the transport of B molecules towards the surface, i.e. it is a relatively rapid process. As soon as the surface has lost all its A molecules,  $\Gamma$  begins to increase again, eventually reaching a new plateau corresponding to full coverage by B. That the exchange step is not rate-determining fits in with the conclusion that attachment is mostly rapid, but it is likely that this is a specific characteristic of the PEO/SiO<sub>2</sub> system. Experiments by Granick and coworkers on exchange between PS and deuterated PS reveal extremely slow processes.<sup>36</sup>

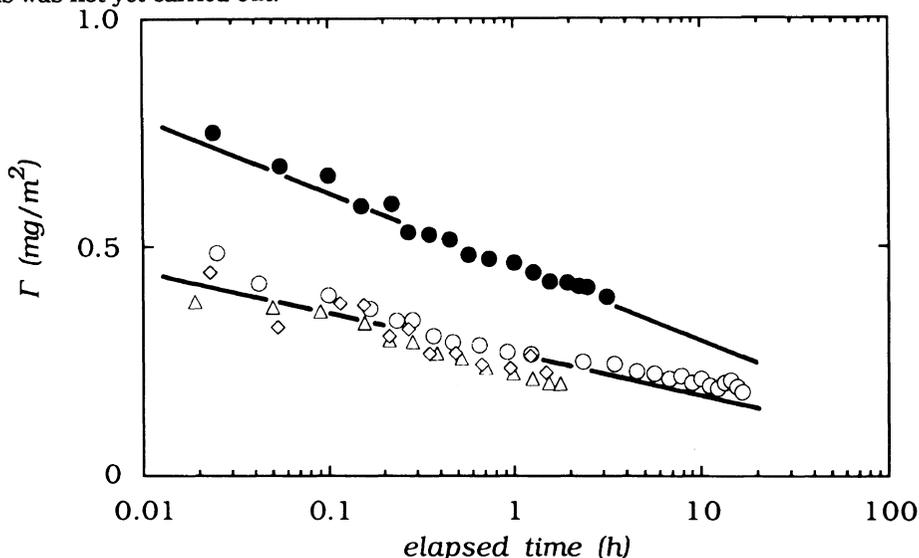
We also studied a case of slow exchange between two different polymers (Poly Butyl Methacrylate, PBMA and Poly Tetra Hydro Furane PTHF) using internal reflection infrared spectroscopy with a cylindrical ATR crystal ('CIRCLE cell'). From preceding experiments<sup>37</sup> it was known that PBMA is more weakly adsorbed than PTHF so that the latter polymer should be able to displace the former. This is confirmed by the experiment. Firstly, upon simultaneous addition of PBMA and PTHF, only PTHF is adsorbed (fig. 14).



**Figure 14.** Adsorption ( $\Gamma$ ) from a mixture of PBMA and PTHF in  $\text{CCl}_4$  on  $\text{SiO}_2$ , as a function of time. Circles: PBMA; triangles: PTHF; diamonds: total adsorption; filled symbols; simultaneous adsorption; open symbols: sequential adsorption.

If PBMA is first introduced into the cell, it adsorbs rapidly. If after a certain lagtime  $\tau$  (here 3.5 hours) PTHF is added, one first observes a rapid adsorption of PTHF, followed by a very slow decrease in the amount of adsorbed PBMA. The rate of PBMA desorption is independent of the PTHF concentration in solution (hence, the rate determining step is at the surface) and seems to follow a  $\log t$  law. Extrapolating the data (see fig. 15) one expects full desorption after about 5 weeks!

Hence the exchange rate depends very strongly on the type of system under investigation: the PS/SiO<sub>2</sub>/CCl<sub>4</sub> and PBMA + PTHF/SiO<sub>2</sub>/CCl<sub>4</sub> systems appear to be very slow, whereas the PEO/SiO<sub>2</sub>/H<sub>2</sub>O system is relatively fast. Also, the lagtime  $\tau$  seems to play a role since the results of the simultaneous experiment ( $\tau=0$ ) and the consecutive one ( $\tau = 3.5$  hours) were very different. Systematic variation of  $\tau$  would be interesting but this was not yet carried out.<sup>37</sup>



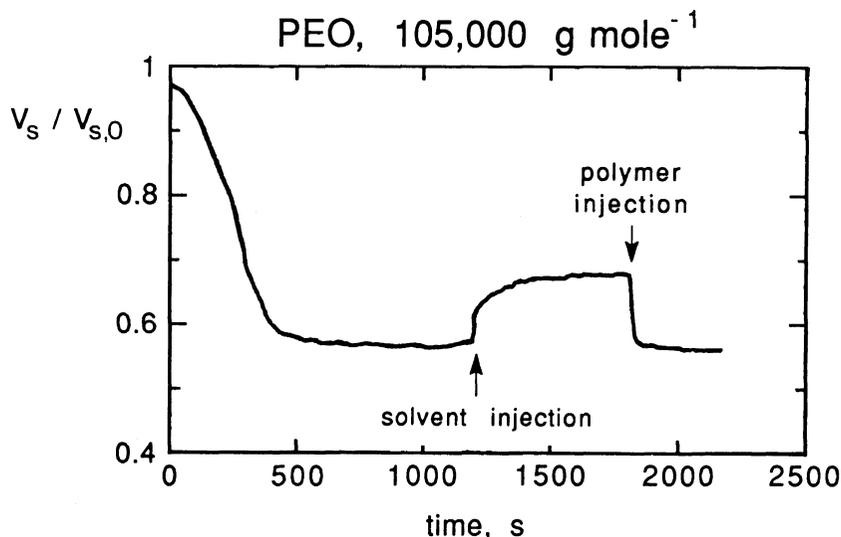
**Figure 15.** Displacement of PBMA by PTHF in CCl<sub>4</sub>. PTHF added after a lag time of 3.5 hours. Open symbols: various PTHF concentrations, PBMA concentration 20 mg/l. Filled symbols PTHF concentration 20 mg/l, PBMA concentration 350 mg/l.

Desorption by pure solvent appeared to be too small to detect by reflectometry, even for the seemingly reversible PEO/SiO<sub>2</sub>/H<sub>2</sub>O system. However if the same experiment is repeated while following the layer thickness instead of the adsorbed mass, appreciable changes are observed. This was done by means of the streaming potential method, and fig. 16 presents an example.

The adsorption process is characterized by an S-shaped curve, which is a somewhat smoothed version of the S-shaped curves for  $\delta_H$  as a function of  $\Gamma$  (fig. 5). The smoothing is due to the fact that the polymers bulk mass transfer rate towards the capillary wall is more rapid at the entrance of the capillary, than at the outlet end. This is expressed by the Lévêque equation:

$$J = 0.855 D^{2/3} c \dot{\gamma}^{1/3} x^{-1/3} \quad (5)$$

where  $x$  is the distance downstream from the capillary entrance and  $\dot{\gamma}$  is the wall shear rate. Calculations show that if the relation between  $\delta_H$  and  $\Gamma$  and that between  $\Gamma$  and time, are combined with Eq. 5, the experimental curves are well reproduced.



**Figure 16.** Reduced streaming potential  $V_s/V_{s,0}$  as a function of time during adsorption and desorption of PEO on the water/SiO<sub>2</sub> interface inside a capillary  $M = 10^5$  g/mole.

When the solution that is pumped through the capillary is replaced by pure solvent, a substantial increase in  $v_s$ , i.e. decrease in  $\delta_H$  is recorded, despite the fact that no desorption was detected by the reflectometer. Again, this is a manifestation of the very steep increase in  $\delta_H$  with  $\Gamma$ ; the quite noticeable decrease in  $\delta_H$  corresponds to a very small decrease in  $\Gamma$ , as predicted by the theory.

#### CONCLUSIONS

Equilibrated adsorption layers of polymers have been well studied and are largely understood. However, the movement of polymer chains in contact with an interface is a relatively new field of study. Wide differences in relaxation times occur, which may be the cause of qualitative differences in behaviour between one system and another. Timescales for individual processes such as attachment, reformation and self diffusion, have not yet been obtained separately, although perhaps exchange studies are a good way to obtain them. Apart from some thoughts on glassy layers<sup>38</sup> and a reptation model<sup>39</sup> there is not much theory yet. Surface specific techniques such as ATR infrared spectroscopy, electrokinetics and optical reflection, as well as kinetic studies of bridging flocculation of colloidal dispersions by polymers appear promising for an experimental approach.

#### REFERENCES

1. D.H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, N.Y. 1983.
2. B. Vincent, *Adv. Colloid Interface Sci.* **4**, 193 (1974).
3. G.J. Fleer, J.M.H.M. Scheutjens and B. Vincent in: 'Polymer Adsorption and Dispersion Stability', Goddard E.D. and Vincent, B. (eds.). ACS Symposium Series 240, p. 245 (1984).
4. J.F. Joanny, L. Leibler and P.G. de Gennes, *J. Pol. Sci Pol. Phys. Ed.* **17**, 1073 (1979).
5. Th.F. Tadros in: 'The effect of Polymers on Dispersion Properties', T.F. Tadros, ed.; Academic Press, London (1982) p. 1.

6. B. Yarar in: 'Solution Behaviour of Surfactants', K.L. Mittal, E.J. Fendler, eds., Plenum Press, N.Y. 1982, Vol. 2, p. 1333.
7. M. Doi, S.F. Edwards, 'The Theory of Polymer Dynamics', Clarendon Press, Oxford (1986).
8. Y. Lipatov, L.M. Sergeeva, 'Adsorption of Polymers', John Wiley & Sons, London, 1974.
10. C.A.J. Hoeve, *J. Chem. Phys.* **44** 1505 (1966).
11. A. Silberberg, *J. Chem. Phys.* **46** 2835 (1968).
12. R.J. Roe, *J. Chem. Phys.* **60** 4192 (1974).
13. J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **83** 1619 (1979).
14. J.M.H.M. Scheutjens, G.J. Fleer, *J. Phys. Chem.* **84** 178 (1980).
15. M.A. Cohen Stuart, T. Cosgrove and B. Vincent, *Adv. Colloid Interface Sci.* **24** 143 (1986).
16. O.A. Evers, J.M.H.M. Scheutjens and G.J. Fleer, *J. Chem. Soc. Faraday Trans.* **86** 1333 (1990).
17. B. van Lent, J.M.H.M. Scheutjens, *Macromolecules*, **22**, (1989) 1931.
18. F.A.M. Leermakers, J.M.H.M. Scheutjens and J. Lyklema, *Biophys. Chem.*, **18**, 353 (1983).
19. M.R. Böhmer, O.A. Evers and J.M.H.M. Scheutjens, *Macromolecules*, **23**, 2288 (1990).
20. T. Cosgrove, *J. Chem. Soc. Faraday Trans.* **86** 1323 (1990).
21. J.M.H.M. Scheutjens and G.J. Fleer in: 'the Effect of Polymers on Dispersion Properties', T.F. Tadros, ed., Academic Press, London (1982) p. 145.
22. C. van der Linden, R. van Leemput, *J. Colloid Interface Sci.* **67**, 48 (1978).
23. J.C. Dijt, M.A. Cohen Stuart, G.J. Fleer, *Colloids Surfaces*, in press (1990).
24. G.P. van der Beek, M.A. Cohen Stuart, T. Cosgrove, *Langmuir*, accepted for publication (1990).
25. T. Cosgrove, B. Vincent, T.L. Crowley and M.A. Cohen Stuart, in: 'Polymer Adsorption and Dispersion Stability', E.D. Goddard and B. Vincent, eds., ACS Symposium Series 240, p. 147 (1984).
26. M.A. Cohen Stuart, F.H.W.H. Waajen, T. Cosgrove and T.L. Crowley, *Macromolecules*, **77** 1825 (1984).
27. M.A. Cohen Stuart, F.H.W.H. Waajen, S.S. Dukhin, *Colloid Polymer Sci.* **262**, 423 (1984).
28. L.K. Koopal, V. Hlady, J. Lyklema, *J. Colloid Interface Sci.* **121**, 49 (1988).
29. M.A. Cohen Stuart and J.W. Mulder, *Colloids Surfaces*, **15**, 49 (1985).
30. J.M.H.M. Scheutjens, G.J. Fleer, *Macromolecules*, **18**, 1882 (1985).
31. E.G.M. Pelssers, M.A. Cohen Stuart, G.J. Fleer, *Colloids Surfaces* **38**, 15 (1989).
32. M. Von Smoluchowski, *Phys. Z.* **17**, 557, 585 (1916).
33. M. Von Smoluchowski, *Z. Phys. Chem.* **29**, 129 (1917).
34. E.G.M. Pelssers, M.A. Cohen Stuart, G.J. Fleer, *J. Chem. Soc. Faraday Trans.* **86**, 1355 (1990).
35. J.G. Petrov, R. Miller, *Colloid Polymer Sci.* **255**, 669 (1977).
36. S. Granick, *J. Phys. Rev. Letters* (submitted).
37. G.P. van der Beek, M.A. Cohen Stuart, G.J. Fleer, *Macromolecules* (submitted).
38. K. Kremer, *J. Physique*, **47**, 1269 (1986).
39. P.G. de Gennes, in 'New Trends in Physics and Physical Chemistry of Polymers; L.H. Lee, ed., Plenum Press, N.Y. (1989) p.1.