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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Pefferkorn, E. , Elaissari, A. and Huguenard, C.(1992) 'Rate Limiting Processes in Diblock Copolymer Adsorption at Solid-Liquid Interfaces', Journal of Macromolecular Science, Part A, 29: 6, 147 — 153

**To link to this Article:** DOI: 10.1080/10101329208054576

**URL:** <http://dx.doi.org/10.1080/10101329208054576>

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## RATE LIMITING PROCESSES IN DIBLOCK COPOLYMER ADSORPTION AT SOLID-LIQUID INTERFACES

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### ABSTRACT

The progress of surface coverage during block copolymer adsorption was investigated by determining the temporal variation of the polymer concentration in the liquid phase surrounding the non-porous adsorbent. Two kinetically different processes were observed. A fast adsorption process stopped after a short period while a slow superadsorption progressively developed over two months. The fast regime was interpreted using computer simulation based on an algorithm of random sequential adsorption. Good correlation between experiments and simulation led to assume that fast adsorption corresponded to a surface coverage close to 40 %. Above this value, adsorption on the remaining free area required large conformational modifications.

### INTRODUCTION

The kinetics of the adsorption of block copolymers from selective solvents onto solid surfaces has been studied theoretically (1,2) and experimentally (3-6). It depends on successive processes leading to the establishment of polymeric brushes on the solid surface. The initial step of surface coverage is concerned with solution to surface mass transfer which is generally governed by the polymer diffusion rate (3). A second rate controlling process is the excluded surface area effect: the anchoring block has to find a free area available for adsorption. This effect becomes important close to completion of surface area filling. A third rate limiting process corresponds to crossing of the diffuse layer constituted by the non adsorbed chain segments of the solubilized block, while a fourth mechanism which may impose unusual slowness is the structural reformation of the adsorbed macromolecules. This study is devoted to an experimental investigation of the phenomena emerging during adsorption. Therefore, the influence of the molecular weight of the polymer is not considered here (6).

The paper consists of two parts. In the first part, the kinetics of the fast adsorption process are analyzed in terms of the excluded surface area, which tends to progressively slow down the adsorption rate. To estimate quantitatively its influence, a simulation of progressive surface occupation is given using an algorithm of random sequential adsorption. Agreement between simulation and experiment shows that excluded area effects may be responsible for "stopping" of the fast adsorption process. It is also shown how the mode of surface filling

may be responsible of the irreversibility for the adsorption and thus assure stabilization of colloidal systems in the presence of block copolymers. In the second part, the kinetic of the unusual slow adsorption process which is observed is discussed, taking into account reformation of adsorbed blocks. In fact, we chose a copolymer characterized by a relatively short non adsorbing sequence (314 chain segments), while the anchoring block contained 771 monomer units.

### MATERIALS

The adsorbent was non porous glass beads of 34 mm average diameter and  $780 \text{ cm}^2/\text{g}$  specific surface area. This adsorbent was treated with hot hydrochloric acid to extract or exchange with  $\text{H}^+$  all surface ionic exchangeable species. The beads were then washed free of acid. Excess water was evaporated under reduced pressure at  $40^\circ \text{C}$  to maintain the fully hydrated silanol surface. Hence the sorbent bore only silanol surface groups, the density of hydroxylic groups being close to  $7.9 \cdot 10^{14} / \text{cm}^2$ .

The copolymer poly-2-vinylpyridine-polystyrene (PVP-PS) was kindly provided by the Ecole d'Application des Hauts Polymères (EAHP-Strasbourg). Synthesis and radiolabeling has been described elsewhere. The specific radioactivity of the  $^{14}\text{C}$  labeled polymer was  $220 \text{ cpm}/\mu\text{g}$  and the solvent toluene was distilled and stored over molecular sieves.

### METHODS

Experimentally, two techniques were employed to determine the adsorption rate during the entire period of surface covering.

Information relative to the relatively fast adsorption regime was obtained by controlling the rate of polymer supply to the solid surface: in this initial stage of fast adsorption, the rate of surface covering was artificially slowed down by using very dilute polymer concentrations in the supernatant solution. When at the end of this process the adsorption rate became slow, the polymer concentration in the liquid phase was increased to take advantage of mass action effects. To determine the retardation due to the polymeric interface, mass transfer from the solution to the interface should be controlled by rapid reproducible mixing conditions to shorten the bulk diffusion step. At the same time, similar conditions should be imposed over a large adsorbent area to obtain quantitative information on the temporal evolution of the surface coverage. These requirements are fulfilled by homogenizing in a reactor a suspension of fine particles dispersed in a liquid phase. Then, the polymer solution is injected into the reactor at a given rate, while small samples of the liquid supernatant are collected and analyzed for polymer concentration. More details are given in reference (7).

Features of the very slow adsorption regime were obtained using the classical procedure of gentle, periodic mixing of polymer and adsorbent over two months. Polymer adsorption was determined by the depletion method. The range below the critical micellar concentration which was investigated requires precise determination of the polymer concentration in the supernatant solution obtained by using a radiolabeled solute. All experiments were performed at  $25^\circ \text{C}$ .

## RESULTS AND DISCUSSION

**Schema of the diblock copolymer in solution**

Toluene constitutes a good solvent for the styrene block and a non-solvent for the pyridine sequence. Below the critical micellar concentration, the solute macromolecule may have a segregated structure where, as usually assumed, the PVP core is protected from precipitation by the polystyrene chain. Strong interactions between silanol surface groups and pyridine groups of the polymer are expected to occur only at short distances in the apolar medium and one may question the capacity for adsorption of the internal core moiety, which is segregated and protected from the solvent (8,9). In the following, we assume that the insoluble PVP sequence may be viewed as a hard sphere, which turns into a flat disk on adsorption.

**Adsorption: a fast process***investigated by experiments*

We previously showed that diffusion effects in solution and in the stagnant layer around each glass bead, which could slow down the adsorption rate, may be neglected under the present experimental conditions (10). In this work, we assume that the interfacial resistance to adsorption is dependent only on the free area available for further adsorption. We define a kinetic coefficient [1], which implies that the number of polymer molecules adsorbed per second depends on the number of molecules already adsorbed and on the polymer concentration in the supernatant solution. To determine the validity of this approach, the temporal variation of the adsorption is determined for different rates of polymer supply to the sorbent. In order to correlate the experimental results with those from simulation, we express the polymer concentration in the solute at time  $t$  in terms of the number  $N$  of molecules per  $\text{cm}^2$  of adsorbent, while in the interface  $N_s$  is the number of polymer molecules adsorbed per  $\text{cm}^2$ . The corresponding relation is as follows:

$$dN_s/dt = N K(N_s) \quad [1]$$

where  $dN_s/dt$  is the adsorption rate and  $K(N_s)$  ( $\text{s}^{-1}$ ) the kinetic coefficient.

Fig. 1 represents the kinetic coefficient  $K(N_s)$  as a function of the amount  $N_s$  of polymer adsorbed for different rates of polymer supply. The validity of eq. [1] is verified in Fig. 1: each point corresponds to the  $K(N_s)$  value calculated in the multiple situations where the polymeric layer bearing the same number  $N_s$  of adsorbed macromolecules per square centimeter is brought into contact with solutions of different concentration  $N$ . The decrease of  $K(N_s)$  expresses the increasing difficulty of finding a free interfacial area available for the solute macromolecule colliding with the surface. One observes that the number of polymer adsorbed is equal to  $1.10 \cdot 10^{12}$   $\text{mol}/\text{cm}^2$ , which corresponds to  $5.4 \cdot 10^{14}$  molecular chain segments of the anchoring PVP block. It should be noted that no further adsorption could be detected over a range corresponding to a fivefold increase of the polymer concentration in the liquid phase. The adsorption process appears to stop: values of the kinetic coefficient drop to  $10^{-4}$  or  $10^{-5}$ , while the number of adsorbed macromolecules tends to stabilize.

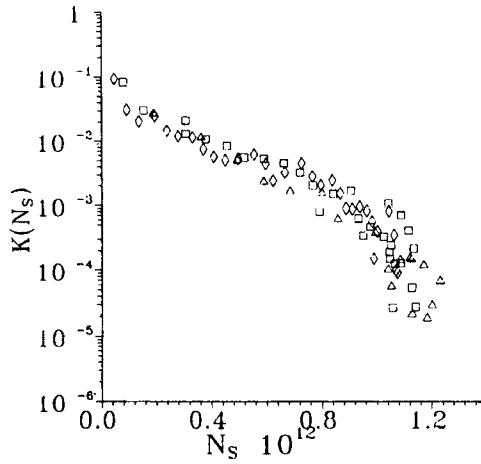


Fig. 1: Adsorption of PVP-PS on silica.  
 Kinetic coefficient  $K(N_s)$  vs  $N_s$  for different rates of polymer supply ( $\text{mol}/\text{min cm}^2$ ): (○)  $2.8 \cdot 10^{-14}$ ; (□)  $4.95 \cdot 10^{-14}$ ; (△)  $12.9 \cdot 10^{-14}$ .

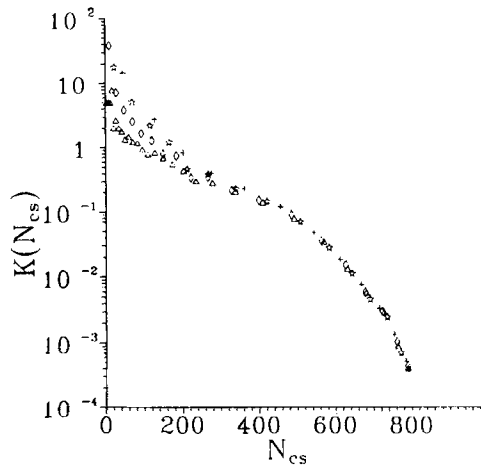


Fig. 2. RSA model.  
 Kinetic coefficient  $K(N_{cs})$  vs  $N_{cs}$  for different rates of disk supply: (△) 5; (○) 20; (□) 50; (+) 100.

*investigated by simulation*

Random sequential adsorption was first used to calculate the maximum coverage when disks are randomly deposited onto a plane and more recently to determine the corresponding rate of surface coverage. Maximum coverage corresponded to a relative surface filling of 0.5472 (11-13). The model assumes that a disk is deposited onto the plane when the corresponding area is free of adsorbed disks. When the randomly selected position is occupied, adsorption does not occur. We use a model which allows deposition of about 1230 disks of radius  $r$  onto a rectangular plane surface of dimensions  $60r$  by  $120r$ .

At time  $t=0$ ,  $\Delta N_c$  disks are placed in the vicinity of the plane. Each disk can carry out only one attempt to adsorb before the time is incremented by  $\Delta t_c$ . Simulation indicates that after one period  $\Delta t_c$ ,  $\Delta N_{cs}$  disks succeed in adsorbing while  $N_c$  disks fail. During a second period  $\Delta t_c$ , the constant number of attempts  $\Delta N_c$  is increased by the number  $N_c$  which failed in the first period. As in the experimental procedure, the non-adsorbed disks remain in the system and again attempt to adsorb during each period  $\Delta t_c$ . Our simulation indicates the new values  $\Delta N_{cs}$  and  $N_c$  after  $(\Delta N_c + N_c)$  attempts. This procedure is continued up to full surface coverage of the plane with disks. We observe that  $\Delta N_c$  rapidly becomes very much smaller than  $N_c$  and that in the calculation of the kinetic coefficient  $K(N_{cs})$  the rate of putting the disks in the vicinity of the plane does not play a role. The time is increased by one unit when all disks have tried once to adsorb. As in eq. [1], the kinetic coefficient is given by:

$$K(N_{cs}) = \Delta N_{cs}/N_c \quad [2]$$

which measures the probability of adsorption onto the plane if  $N_{cs}$  disks are previously adsorbed at random.

Fig. 2 portrays the kinetic coefficient  $K(N_{cs})$  as a function of  $N_{cs}$  for different values of  $\Delta N_c$ , the rate of disk supply. One observes that the unique curve obtained over a large range of surface coverages displays the characteristic variation of  $K(N_s)$  in Fig. 1. The kinetic coefficient could not be determined for adsorption of more than 800 disks. Nevertheless, it appears that the adsorption rate leading to full coverage with up to 1230 disks brings into play very small  $K(N_{cs})$  values. As 1230 disks occupy 0.547 % of the available area, one notes that it is very time consuming to cover an area larger than about 40 %.

Considering this result, one has to conclude that at the end of the fast adsorption regime, the area occupied by the adsorbed polymer is smaller than one half of the geometric area of the sorbent. This is due to the random deposit of disks or macromolecules, which are irreversibly adsorbed. The reason for the permanent localization of the adsorbed macromolecules lies in the fact that 400 to 500 silanol groups of the adsorbent oppose the 771 pyridine groups of an adsorbed PVP block. Strong interactions are thus expected to occur similar to those in complex polyanionic-polycationic systems and irreversibility of adsorption would be expected.

This surface occupation may be schematically represented by a collection of adsorbed disks of radius 4 nm. When compared to the radius of gyration of a polymer chain in  $\theta$ -solvent (15 nm), this value indicates the existence of a collapsed state of the PVP block at the interface.

**Adsorption: a very slow process**

We found that the end of the fast adsorption regime did not constitute a state of thermodynamic equilibrium. In Fig. 3 the number  $N_s$  of polymer adsorbed is

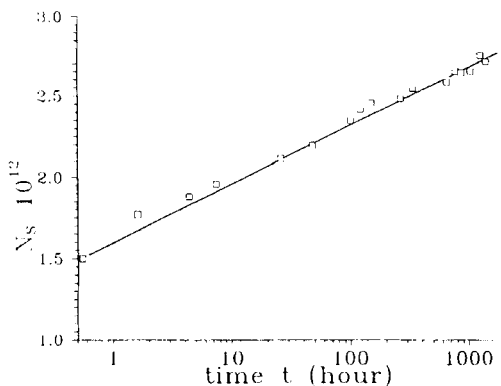


Fig.3. Representation of the number of copolymer adsorbed  $N_s$  (mol/cm<sup>2</sup>) as a function of log time for PVP-PS (771-314): slow adsorption regime.

represented as a function of the logarithm of the incubation time. We see that superadsorption starts from the situation of half surface coverage with about  $1.1 \cdot 10^{-12}$  mol/cm<sup>2</sup>. Fig. 3 shows that the slow increase of the amount adsorbed  $\Delta N_s$  (mol/cm<sup>2</sup>) over a period of one hour may be expressed by the empirical relation:

$$\Delta N_s = 0.18 \cdot 10^{-12}/m \quad [3]$$

where  $m$  represents the incubation time in hours. After a period of two months, the number of adsorbed polymers per square centimeter is  $2.7 \cdot 10^{-12}$ . This value corresponds to full coverage of the surface if one assumes that  $1.1 \cdot 10^{-12}$  mol/cm<sup>2</sup> corresponds to a relative coverage of 40 %.

The analysis based on results of random sequential adsorption is now slightly different from the previous case, where full coverage of the surface was assumed at the end of the fast adsorption process. Complementary interpretation of the slow regime may be given. It is obvious that excluded surface effects may slow down the adsorption rate, as observed in simulation. On the other hand, we find that the radius of an adsorbed disk is comparable to the calculated value of the radius of gyration of polystyrene having a polymerization index of 177. This interfacial layer may also contribute to slow down the adsorption rate: according to theoretical predictions  $N_s$  is expected to increase with  $\log t$ . However, distinction of the relative influence of these two rate limiting phenomena is not yet possible.

## CONCLUSIONS

Use of radiolabeled polymers allowed precise determination of the adsorption kinetics when the interfacial layer was formed by copolymer adsorption below the critical micellar concentration. Fast and slow kinetics were observed.

In the fast regime, the anchoring block adsorbed by forming a flat carpet of pyridine segments strongly interacting with the silica silanol groups. Simulation of the covering process by a random sequential adsorption model led us to conclude that at the end of the fast regime, the polymer layer occupied only 40 % of the surface.

In the slow regime, a significant increase of adsorption was recorded. In fact, the copolymer interface would require an infinitely long time to reach full surface coverage.

The development of the adsorption process described in the present paper is valid for a copolymer of specific polymerization indexes. Its main characteristic is that it is able to build a monolayer of pyridine segments in the interface. For copolymers with a higher polymerization index of the pyridine block, we found that flat monolayers are not formed and that, even in the fast adsorption regime, the thickness of the adsorbed disks increases with the polymerization index.

## ACKNOWLEDGEMENTS

Dr J.M. Widmaier is acknowledged for furnishing the copolymer sample. This work was supported through the project 936 GDR "Mesures des forces de surfaces" of the CNRS.

## REFERENCES

1. Johner, A., and Joanny, J.F., *Macromolecules* 23, 5299 (1990).
2. Tassin, J.F., Siemens, R.L., Tang, W.T., Hadziioannou, G., Swalen, J.D., and Smith, B.A., *J. Phys. Chem.* 93, 2106 (1989).
3. Motschman, H., Stamm, M., and Toprakcioglu, C., *Macromolecules* (In Press).
4. Munch, M.R., and Gast, A.P., *J. Chem. Soc. Faraday Trans.* 86, 1341 (1990).
5. Leermakers, F.A.M., and Gast, A.P., *Macromolecules* 24, 718 (1991).
6. Huguenard, C., Varoqui, R., and Pefferkorn, E., *Macromolecules* 24, 2226 (1991).
7. Pefferkorn, E., Haouam, A., and Varoqui, R., *Macromolecules* 21, 2111 (1988).
8. Pefferkorn, E., Tran, Q., and Varoqui, R., *J. Polym. Sci.: Polym. Chem. Ed.* 19, 27 (1981).
9. Paronage, E., Tirrel, M., Watanabe, H., and Nuzzo, R., *Macromolecules*, 24, 1987 (1991).
10. Pefferkorn, E., Carroy, A., and Varoqui, R., *Macromolecules* 18, 2252 (1985).
11. Feder, J., and Giaever, I., *J. Colloid Interface Sci.* 78, 144 (1980).
12. Onoda, G.Y., and Lininger, E.G., *Phys. Rev. A* 33, 715 (1986).
13. Schaaf, P., and Talbot, J., *Phys Rev. Lett.* 62, 175 (1989).