

# **EXCHANGE OF CATIONIC POLYMERS ADSORBED ON CELLULOSE FIBERS AND ON MONODISPERSE POLYSTYRENE LATEX**

Hiroo Tanaka

Department of Forest Products, Kyushu University, Fukuoka 812, Japan

Lars Ödberg

Swedish Pulp and Paper Research Institute, Box 5604, S-114 86  
Stockholm, Sweden

## **ABSTRACT**

Two series of cationic polyacrylamides (C-PAM) were prepared, with and without fluorescent labelling, one with constant charge density (CD:1.4 meq/g) and different molecular weights (MW:2x10<sup>4</sup>, 4x10<sup>5</sup> and 8x10<sup>6</sup>) and one with constant molecular weight (4x10<sup>5</sup>) and different charge densities (CD:0.65 meq/g, 1.4 meq/g and 2.5 meq/g).

The exchange reactions of these C-PAMs on monodisperse polystyrene latex (PSL) and cellulose fibers have been studied using C-PAMs with the same MW and CD except that the pre-adsorbed polymers were fluorescently labelled. The first series of experiments was carried out near the saturation level of the pre-adsorbed polymers. For C-PAMs with the highest MW(8x10<sup>6</sup>) no significant exchange could be detected on PSL or on fibers. When C-PAM with the highest CD (2.5 meq/g) was used a slight exchange occurred on both PSL and fibers. The exchange became more extensive with decreasing MW and CD. The exchange reactions initially proceeded quite rapidly and then slowed down. The initial exchange was more extensive on cellulose fibers than on PSL, probably because of the lower surface CD of the fibers, but it levelled off more rapidly than on PSL. This difference is most probably an effect of the porous structure of the fibers.

The pre-adsorption levels of the polymer were then reduced from their saturation values to examine the conformational change of the polymer after adsorption and/or the mode of penetration of the polymer into the pores of fibers. In these experiments, the effect of the time between adsorption and displacement was studied. On PSL the level of exchange was influenced only slightly by the time before displacement started, and after 2 hours there was no further reduction in desorption. On cellulose fibers, on the other hand, the levels of exchange were affected significantly by the time before displacement began, and the decrease in exchange continued even after 3 weeks. The rates and levels of exchange were also influenced by the molecular weights and charge densities.

## INTRODUCTION

Studies of polymer exchange reactions on solid surfaces should provide insight into the processes occurring during the adsorption of polymers and also give a better understanding of polymer-induced stability and flocculation in colloidal systems. In the papermaking field, studies of polymer exchange reactions should give insight into the mechanism of polymeric retention and drainage aids as well as the mechanism of paper strength additives.

Polymer exchange reactions should take place when the segment-surface binding energies of displacing polymers are higher than those of adsorbed polymers (1,2). The preferential adsorption of high molecular weight species of non ionic polymers has also been reported (3-9). A small fraction of radioactively labelled non ionic polyacrylamide loosely attached to non porous glass beads exchanged very slowly with unlabelled molecules (10).

Studies on the exchange of polyelectrolytes are however very limited. Bain et al (11) reported that sodium polyacrylates or sodium carboxymethyl celluloses with low MW were preferentially adsorbed onto barium sulfate and were not displaced by a high MW polymer even after 71 days. Adam and Robb (12) obtained similar results on calcium carbonate. Wright et al (13) reported that no significant desorption from barium sulfate occurred when polyacrylate was both the adsorbed and displacing species and the dispersion medium was water without added electrolyte. Significant desorption occurred however in

0.1 mol/l NaCl if the displacing polyacrylate had a higher MW than that being desorbed.

Studies have so far been undertaken only for non ionic and anionic polymers. The behaviour of cationic polymers on anionic surfaces are particularly interesting from a practical point of view since most natural surfaces have an anionic character.

The purpose of the present investigation has been two-fold. Firstly the exchange reactions of C-PAM on monodisperse polystyrene latex (PSL) and on cellulose fibers have been studied using fluorescently labelled and unlabelled polymers with different molecular weights and charge densities. Secondly the penetration of C-PAMs into pores in cellulose has been investigated by observing the effect of the time between adsorption and displacement on the polymer exchange reactions.

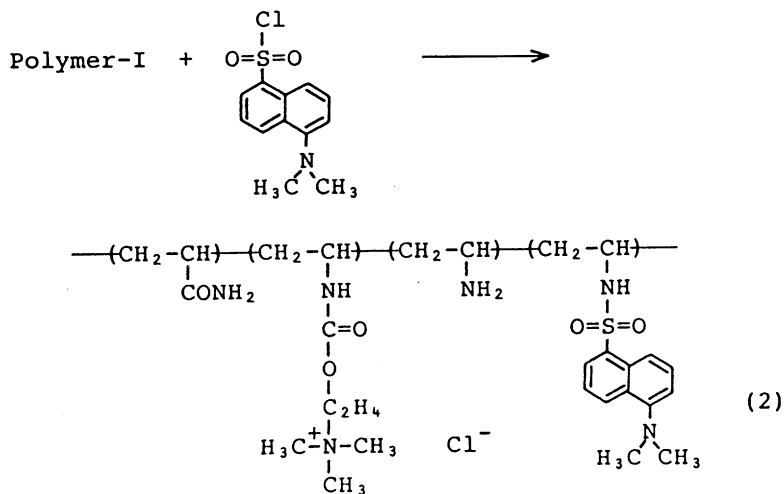
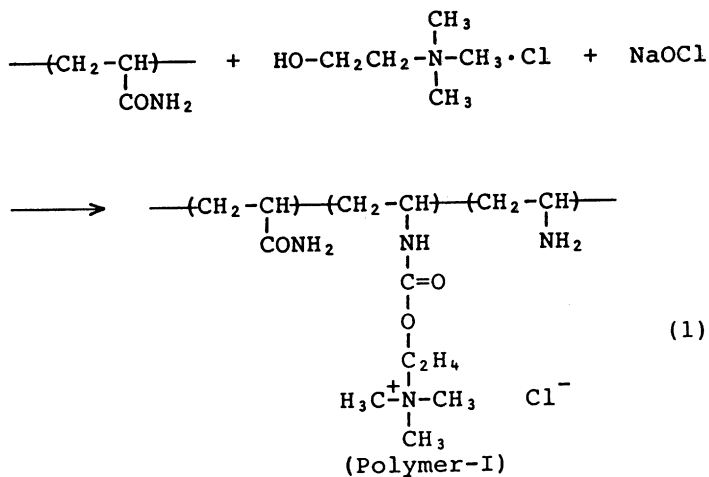
## **EXPERIMENTAL**

### **Materials**

Polyacrylamides (PAM) with high and medium MW's were prepared in aqueous solution using the  $K_2S_2O_8$ -isopropanol initiator under a nitrogen atmosphere. For the relatively low MW polymer, the acrylamide was polymerized in ethanol under a nitrogen atmosphere with N,N-azobisisobutyronitrile as initiator.

The cationization of PAMs was performed by the Hofmann reaction in the presence of choline chloride. The reactions taking place are shown in Equation (1).

The polymers obtained were slightly dansylated (fluorescently labelled) in a homogeneous system using aqueous dimethylformamide as solvent according to Equation (2). A detailed description will be given elsewhere (14). The characteristics of C-PAM and dansylated C-PAM(DC-PAM) are listed in Table 1. The dansylated compounds are indicated by an asterisk, e.g. P\*2, is the dansylated version of P2.



PSL was synthesized according to (15). The products were monodisperse latex with diameter of 925 nm as determined by electron microscopy. The charge density determined by conductometric titration was 3.5  $\mu\text{eq/g}$  (5.46  $\mu\text{C/cm}^2$ ). The cellulose fibers used were from a never-dried bleached softwood kraft pulp, Imperial Anchor (Iggesund AB, Sweden). The fine material was removed before use. The charge density of the pulp as measured by conductometric titration (16) was 29  $\mu\text{eq/g}$ .

Code	Fluorescence	25 °C [ $\eta$ ]	Molecular weight		Charge density (meq/g)
			1MNaCl	+1 +2	
P1	N	0.19	$1.7 \cdot 10^4$	$2.9 \cdot 10^4$	1.43
P*1	Y	0.17	$1.4 \cdot 10^4$	$2.5 \cdot 10^4$	1.41
P2	N	1.60	$3.4 \cdot 10^5$	$5.4 \cdot 10^5$	0.66
P*2	Y	1.71	$3.7 \cdot 10^5$	$5.8 \cdot 10^5$	0.64
P3	N	1.55	$3.2 \cdot 10^5$	$5.2 \cdot 10^5$	1.38
P*3	Y	1.59	$3.4 \cdot 10^5$	$5.3 \cdot 10^5$	1.42
P4	N	1.43	$2.9 \cdot 10^5$	$4.6 \cdot 10^5$	2.45
P*4	Y	1.55	$3.2 \cdot 10^5$	$5.2 \cdot 10^5$	2.50
P5	N	12.5	$6.1 \cdot 10^6$	$9.0 \cdot 10^6$	1.40
P*5	Y	13.5	$6.7 \cdot 10^6$	$10.0 \cdot 10^6$	1.49

+1 From  $[\eta]_{\text{dl/g}}^{25 \text{ }^\circ\text{C, 1M NaCl}} = 1.91 \cdot 10^{-4} \overline{M_w}^{0.71}$  for PAM (Ref. 19)

+2 From  $[\eta]_{\text{dl/g}}^{25 \text{ }^\circ\text{C, 1M NaCl}} = 1.05 \cdot 10^{-4} \overline{M_w}^{0.73}$  for AM-CMA (30 %) (Ref. 19).

Hereafter the molecular weights of P1(P\*1), P2(P\*2)-P4(P\*4) and P5(P\*5) are simply given as  $2 \cdot 10^4$ ,  $4 \cdot 10^5$  and  $8 \cdot 10^6$  respectively.

**Table 1** Properties of cationic polyacrylamides.

## Procedures

All adsorption and exchange experiments were carried out in deionized water at room temperature ( $22 \pm 1$  °C) under continuous shaking.

In the first part of the experiments, adsorption was carried out so as to allow about 40 % of the added DC-PAM, according to data reported earlier (17), to be adsorbed on PSL or fibers. The contact time between DC-PAM and PSL was 2-3 hours. In the case of fibers times from one day to two weeks were used, depending on the MW and CD of polymer, to reach close to saturation.

After adsorption the PSL, except in the case of the PSL-DC-PAM (MW:  $8 \times 10^6$ ) system, was filtered using a membrane with average pore diameter of 0.6  $\mu\text{m}$  and washed with deionized water until no fluorescence was detected in the filtrate. The aqueous suspension of the resulting PSL had a solids content of 1.44 %. The cellulosic fibers treated by DC-PAM were filtered using a membrane with 3  $\mu\text{m}$  pore diameter and washed extensively. The aqueous suspensions of the fibers had a solids content of 0.6 %. In the case of the PSL-DC-PAM MW ( $8 \times 10^6$ ) system, the PSL with adsorbed polymer was centrifuged at 10,000 rpm for 30 minutes in a Beckman L 5-40, decanted and soaked in water. This procedure was repeated until no fluorescence was detected in the supernatant.

In the later part of this investigation lower addition levels of DC-PAMs were used, 0.22 % on PSL and 0.5-0.65 % on fibers. The mixtures were shaken for various periods from 5 minutes to 3 weeks. After adsorption, the washing procedures were carried out as described above which required 10-15 minutes. The amounts of adsorbed polymer were determined by colloid titration (18) and from the residual fluorescence intensity of the filtrate or the supernatant.

In the exchange experiment, 10 ml of aqueous solution of unlabelled C-PAM with the same MW and CD as the adsorbed DC-PAM was added to 50 ml of 1.44 % PSL or 0.6 % fiber suspension. The molar ratio of C-PAM to DC-PAM was 10:1 when the adsorbates were saturated by DC-PAM. The suspension was shaken, and 3-4 ml of suspension was withdrawn at appropriate time intervals and filtered or centrifuged for complete sepa-

ration. The fluorescence intensity in this filtrate or supernatant was measured using a Perkin-Elmer LS-5 or Hitachi F 3010 Luminescence spectrometer. The excitation and emission wavelengths used were 333 nm and 538 nm respectively, as described previously (14). The desorbed amounts of DC-PAM were determined by comparing the intensities with the calibration curves. These values were corrected for a weak fluorescence intensity of unlabelled polymers (C-PAM).

## RESULTS AND DISCUSSION

### Exchange reaction of C-PAM on PSL: Effect of molecular weight and charge density

PSL was first saturated with DC-PAM. Reaction conditions and results for the adsorption of DC-PAM, and conditions for polymer exchange on PSL are shown in Table 2. Fig. 1 shows the results of the polymer exchange reactions for combinations of the same molecular species except that the pre-adsorbed polymers were fluorescently labelled. C-PAMs with three different MW's ( $2 \times 10^4$ ,  $4 \times 10^5$  and  $8 \times 10^6$ ) but with very similar CD's (1.4 meq/g) were used. Fig. 2 shows the results for C-PAMs with three different CD's (0.65, 1.4 and 2.5 meq/g) and with very similar MW's ( $4 \times 10^5$ ). When no displacer was present, practically no desorption could be detected for any of the polymers.

Code	Initial conc. of DC-PAM (mg/l)	Conc. of DC-PAM at equilibrium (mg/l)	DC-PAM adsorbed on PSL (mg/g)	Conc. of C-PAM as displacer (mg/l)	$\frac{\text{C-PAM}}{\text{DC-PAM}}$ (charge ratio)
P*1	87	51	3.0	355	10
P*2	235	141	7.8	910	10
P*3	86	49	3.1	380	10
P*4	50	30	1.7	205	10
P*5	85	52	2.7	345	10

**Table 2** Conditions and results for adsorption of DC-PAM and conditions for polymer exchange on PSL. PSL: 1.2 %,  $22 \pm 1$  °C, pH: 4.5-5.0

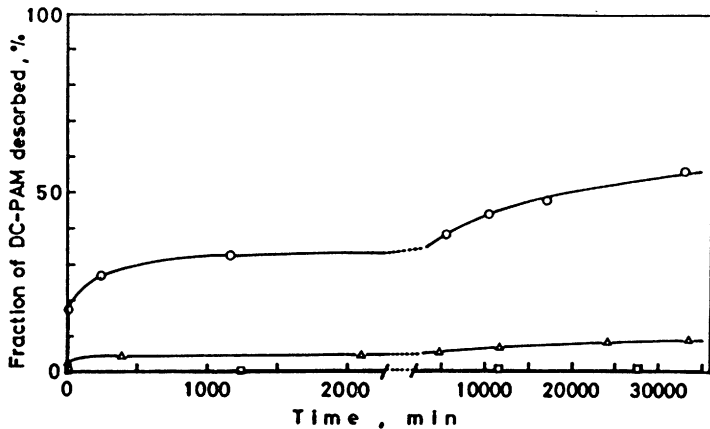


Fig. 1 The fraction of desorbed fluorescently labelled poly-electrolyte, DC-PAM, on PSL for various molecular weights. Reaction conditions see Table 2.  $\circ$  P\*1-P1,  $\Delta$  P\*3-P3,  $\square$  P\*5-P5

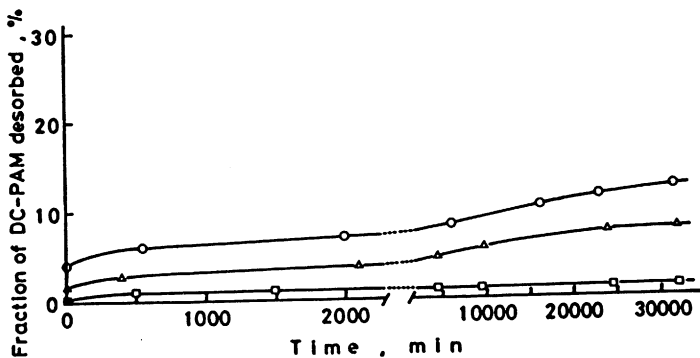


Fig. 2 The fraction of desorbed fluorescently labelled poly-electrolyte, DC-PAM, on PSL for various charge densities. Reaction conditions see Table 2.  $\circ$  P\*2-P2,  $\Delta$  P\*3-P3,  $\square$  P\*4-P4



In the case of the polymer with the highest MW(P\*5), no desorption can be detected even when displacer polymer is present. This lack of exchange agrees with previous investigations (12) and may be explained by the following simple considerations. Firstly, the fact that the number of charges per molecule for P\*5 is of the order of  $1 \times 10^4$  means that every chain may have as many linkages as this to the surface. It is highly unlikely that all these linkages will be broken at the same time, especially in the case when no polymer that can compete for these surface sites is present in solution. Secondly, the interaction between the charged segments of the polymer and the PSL- surface is of an electrostatic nature and thus gives a very strong binding. In the exchange reactions with medium MW(P\*3) and low MW(P\*1) polymer, a considerable desorption can be detected. For P\*3, 9 % may be desorbed over a period of 40 days and for P\*1, 55 % may be desorbed after 30 days. For both polymers there is a high initial desorption but the process continues even after 40 days.

As can be seen in Fig. 2 for the polymers with medium MW ( $5 \cdot 10^5$ ), the polymer (P\*4) with the highest CD (2.5 meq/g) only exchanged slightly. For P\*2 with low CD (0.65 meq/g), 15 % may be desorbed after 30 days.

The number of charges on P\*4, P\*3, P\*2 and P\*1 and hence the numbers of possible linkages per molecules are approximately 1000, 500, 250 and 20 respectively. Figs. 1 and 2 show that polymer exchange reactions occurred much more easily with a decreasing number of possible linkages. Thus these numbers can explain why these polymers are exchanged when P\*5 is not, and they may also explain the difference in exchange between P\*4, P\*3, P\*2 and P\*1.

Several factors may contribute to the shape of the exchange curves. There is probably a distribution of conformations of the polymers on the surface and some polymers with a higher number of interacting segments may be firmly anchored to the surface. The probability of desorbing these polymers will be low and a long time will be needed before they are exchanged with polymers in solution. These firmly anchored polymers are probably those that were first attached to the surface. A second factor, though less important in the present case where the excess of unlabelled polymer is very large, is

that desorbed fluorescently labelled polymers may start to exchange with unlabelled polymers on the surface. This will result in a slower apparent exchange rate when the concentration of desorbed labelled polymers becomes high.

It is not believed that surface roughness will contribute to the slow release over such a long period of time. Since the polymer molecules, P3(P\*3) and P1(P\*1), have estimated sizes of 50 nm and 15 nm respectively (17), the PSL particles, with diameter of 925 nm, should appear as a large smooth surface to the approaching molecules.

The results obtained suggest that although the polyelectrolyte interacts with many charged groups on the surface the situation is dynamic and the polymer is constantly rearranging itself. One or more of the binding sites may start interacting strongly with an approaching molecule in solution and this approaching molecule may gradually occupy more binding sites and eventually displace the originally adsorbed molecule. This process is however extremely slow for high MW polymers.

Code	Initial conc. of DC-PAM (mg/l)	Conc. of DC-PAM at equilibrium (mg/l)	DC-PAM adsorbed on PSL (mg/g)	Conc. of C-PAM as displacer (mg/l)	C-PAM DC-PAM (charge ratio)
P*1	335	187	29.6	1460	10
P*2	650	392	51.6	2500	10
P*3	190	109	16.2	835	10
P*4	55	33	4.4	225	10
P*5	75	45	6.0	320	10

**Table 3** Conditions and results for adsorption of DC-PAM and conditions for polymer exchange on cellulose fiber. Cellulose fiber: 0.5 %, 22± 1 °C, pH: 4.5-5.0.

### Exchange reaction of C-PAM on cellulosic fiber: Effect of molecular weight and charge density

First fibers were almost saturated with DC-PAM. Conditions of the exchange reaction are shown in Table 3. The results of exchange reactions of C-PAMs on fibers are given in Figs. 3 and 4 which show the effect of MW and CD respectively.

A slight exchange reaction, less than 1 % exchange, of the highest MW polymer (P\*5) occurred in the presence of P5, which suggests that some weakly adsorbed P\*5 polymers are present on the fibers. The exchange of polymer with medium MW(P\*3) also took place more easily on fibers than on PSL. Fig. 3 shows that the degree of exchange on fiber reached 25 % after 10 days compared to 7 % on PSL. However, the degree of exchange levelled off close to 25 %. The exchange of polymer with low MW(P\*1) initially occurred quite easily but levelled off close to 47 % after 2 days, as seen in Fig. 3.

Fig. 4 shows that the exchange reaction took place more easily with decreasing CD. For the polymer with the lowest CD (0.65 meq/g) the exchange reactions occurred rapidly at the initial stage. The degree of exchange exceeded 50 % after 18 hours and levelled off close to 60 % after 5 days.

The exchange phenomena on fibers differ from those on PSL. The difference most probably originates in the different surfaces. In our previous work (17), it was found that the adsorption equilibrium of C-PAMs onto PSL was achieved almost instantaneously after mixing whereas equilibrium on cellulosic fibers was reached after a few hours up to several weeks depending on the MW and CD. This indicates that the penetration of polymers into the pores is restricted but once inside the pores the polymers are difficult to exchange. On the other hand, the polymers adsorbed on outer surfaces of cellulosic fibers are easier to exchange than those on PSL because of a weaker interaction, as estimated from the charge densities of cellulose fibers ( $1.4 \mu\text{C}/\text{cm}^2$ ) and PSL ( $5.46 \mu\text{C}/\text{cm}^2$ ).

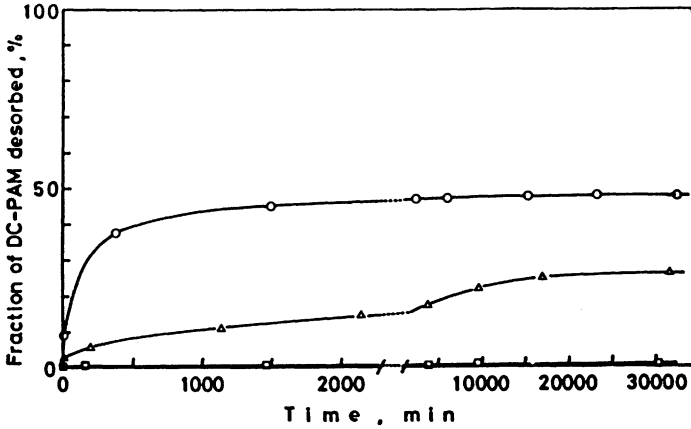


Fig.3 The fraction of desorbed fluorescently labelled poly-electrolyte, DC-PAM, on cellulose fiber for various molecular weights. Reaction conditions see Table 3.

○ P\*1-P1, △ P\*3-P3, □ P\*5-P5

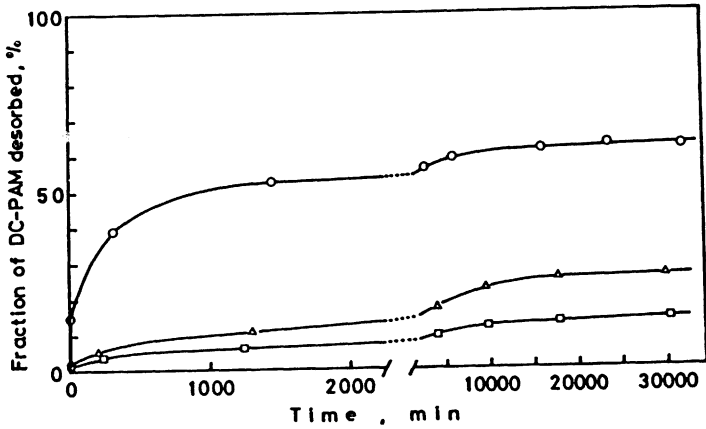


Fig.4 The fraction of desorbed fluorescently labelled poly-electrolyte, DC-PAM, on cellulose fiber for various charge densities. Reaction conditions see Table 3.

○ P\*2-P2, △ P\*3-P3, □ P\*4-P4

## Effect of time between adsorption and displacement on polymer exchange reaction.

Experiments discussed so far were carried out near the saturation level of C-PAM on the solid surfaces. It is from a theoretical and also practical point of view of great interest to investigate the exchange reactions at lower adsorbed amounts. The levels of addition of polymer in the wet end of the paper machine are generally much lower than the saturation level. The complicated exchange reaction on cellulose fiber can be attributed to the penetration of polymer into the pores. Thus the effect of the time between adsorption and displacement was studied.

For PSL, the levels of exchange were considerably reduced when the addition level of C-PAM (P\*1) was lowered, as seen in Fig. 5. The effects of time between adsorption and displacement are shown in Fig. 6. In this experiment, the concentration of displacer (P1) was raised to the same as that of fibers (Fig. 7) to obtain a clearer difference. The degree of exchange was slightly reduced with increasing time between adsorption and displacement in the initial period, but no difference in the exchange reaction could be detected for times of 2 hours and 1 week. An adsorbed polymer molecule has an extended conformation in the earliest stage of adsorption with a limited number of points of attachment. At this stage the exchange may occur with relative ease. As the polymer conformation with time comes closer to a flat equilibrium conformation the exchange becomes more difficult. Results in Fig. 6 shows that the conformational change is complete within 2 hours.

Figs. 7 and 8 show the effects of the time between exchange and displacement on the exchange on fibers. The levels of addition of DC-PAMs (5.2 mg/g for P\*1 (Fig. 7) and 6.5 mg/g for P\*2 (Fig. 8)) were 1/6 and 1/8 of the saturation level (31 mg/g for P\*1 and 52 mg/g for P\*2) respectively.

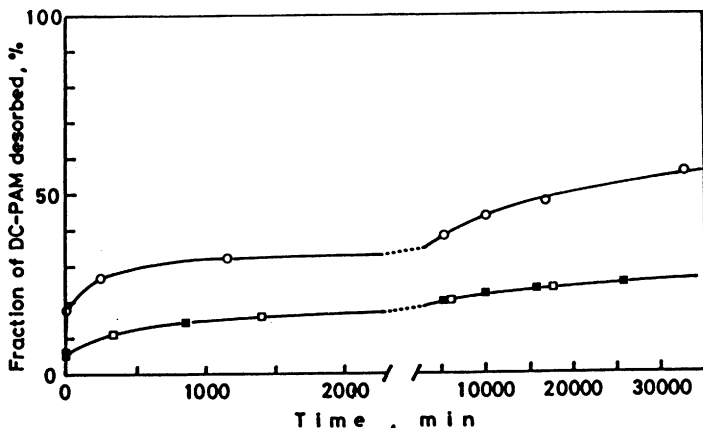


Fig. 5 Effect of addition level of pre-adsorbed DC-PAM on polymer exchange reaction on PSL.

PSL:1.2 %, pre-adsorbed P\*1: ○ 3.0 mg/g, □ 2.2 mg/g

P1:355 mg/l,  $22 \pm 1^\circ\text{C}$ , pH  $4.5 \pm 0.3$

Time between adsorption and displacement

○ □ 3 hr. ■ 24 hr.

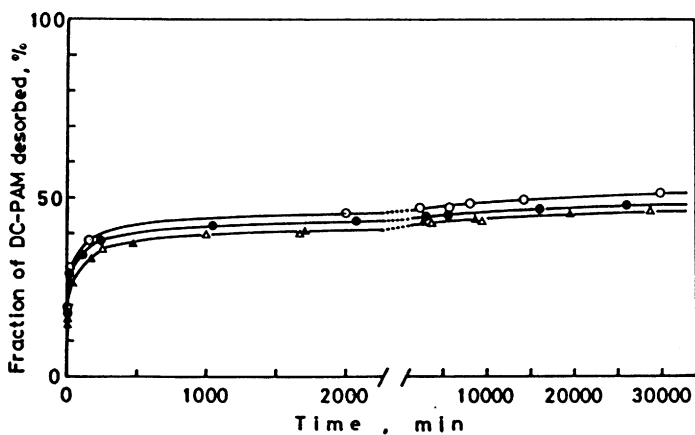


Fig. 6 Effect of time between adsorption and displacement on polymer(P1) exchange reaction on PSL.

PSL:1.2 %, pre-adsorbed P\*1:2.2 mg/g on PSL, P1:1460 mg/l  
 $22 \pm 1^\circ\text{C}$ , pH  $5.5 \pm 0.3$

Time between adsorption and displacement

○ 5 min. ● 50 min. △ 2 hr. ▲ 1 week

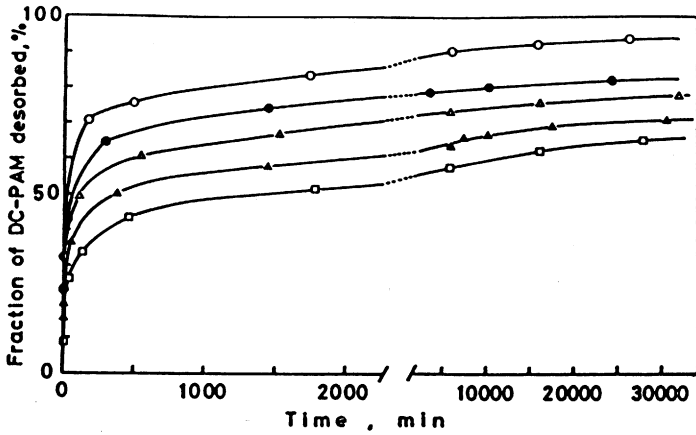


Fig.7 Effect of time between adsorption and displacement on polymer(P1) exchange reaction on cellulose fibers.

Fibers:0.5 %, pre-adsorbed P\*1:5.2 mg/g on fibers,  
P1:1460 mg/l,  $22 \pm 1^\circ\text{C}$ ,  $\text{pH } 5.5 \pm 0.3$

Time between adsorption and displacement

○ 5 min. ● 1 hr. △ 15 hr. ▲ 1 week, □ 3 weeks

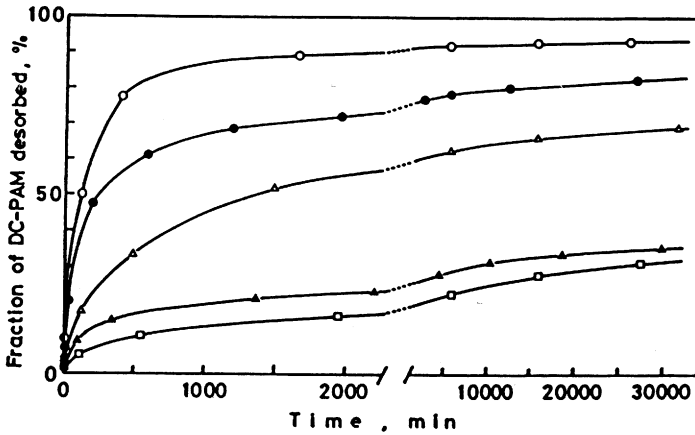


Fig.8 Effect of time between adsorption and displacement on polymer(P2) exchange reaction on cellulose fibers.

Fibers:0.5 %, pre-adsorbed P\*2:6.5 mg/g on fibers,  
P2:2500 mg/l,  $22 \pm 1^\circ\text{C}$ ,  $\text{pH } 5.5 \pm 0.3$

Time between adsorption and displacement

○ 5 min. ● 1 hr. △ 15 hr. ▲ 1 week, □ 3 weeks

For P\*1 (MW:  $2 \times 10^4$ , CD: 1.4 meq/g) when the time before displacement was 5 minutes, the degrees of exchange were 80 % after 16 hours and 94 % after 20 days. With an increase in this time the polymer exchange was retarded gradually and the degrees of exchange were 47 % after 16 hours and 65 % after 20 days when the time between adsorption and displacement was 3 weeks. It is obvious from the results shown in Fig. 7 that the retardation continues even after 3 weeks.

The difference in effect of the time before displacement was even larger when P\*2 with higher MW but lower CD (MW:  $4 \times 10^5$ , CD: 0.65 meq/g) than P\*1 was used. The exchange of P\*2 is more difficult than that of P\*1 in the earliest stage because the number (250) of charged groups on polymer P\*2 is higher than that (20) on P\*1. However, the degree of exchange of P\*2 exceeded that of P\*1 after three and half hours and finally reached the same level (95 %) when the time before displacement was 5 minutes. These results clearly suggest that P\*2 with higher MW is located more on the outer fiber surface, while P\*1 with lower MW can penetrate into the porous fiber wall. With increased time the exchange reactions became much more difficult. Only 13 % of P\*2 had exchanged after 16 hours when the time between adsorption and displacement was 3 weeks, while 87 % of the same polymer exchanged when the time was 5 minutes. Before the experiment, we did not expect that the penetration of the cationic polymer into pores of anionic fibers could continue for more than 3 weeks and dramatically influence the exchange reaction.

## CONCLUSIONS

The results show that the exchange of polymers on surfaces depends not only on the molecular weight but also on the charge density and conformation of the polymers. The surface characteristics are of course also of great importance. From our present and previous data (17) it can also be concluded that both conformational change and penetration of polymer into the pores of cellulosic fibers influence the exchange reactions in the early stage of adsorption, but the penetration is the dominant factor for the reduced exchange when the displacer is added later than ten minutes after adsorption. The fact that an exchange does indeed occur indicates that the polymers adsorbed are in a state of dynamic equilibrium.



**ACKNOWLEDGEMENT**

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## Transcription of Discussion

# EXCHANGE OF CATIONIC POLYMERS ADSORBED ON CELLULOSE FIBRE AND ON MONODISPERSE POLYSTYRENE LATEX

H. Tanaka and L. Odberg

**P. Howland, Portals Ltd UK**

Have you carried out any experiments to see how temperature affects the rate at which the polymers desorb?

**Tanaka, H.**

No, we have not - our experiments were carried out at room temperature 22 degrees centigrade. I think such an experiment would be very interesting.

**Dr. J. Marton SUNY (USA)**

I wonder whether some of the adsorption differences on the smooth polystyrene and the porous cellulose surface cannot have been caused by hydrogen bonding on the latter between the cellulose and the amide groups of the polyacrylamide.

**Tanaka, H.**

The main driving force of adsorption in this case is electrostatic interaction.

**Dr. J. Marton**

No question about that. However there is a major difference between the adsorption capacity of the two surfaces. I wonder whether we should not expect some contribution from this additional effect?

**Tanaka, H.**

The ratio of charge on polymer to polystyrene latex is 1.2 to 1.5 in spite of molecular weight. When we use a polymer with higher molecular weight the polymer cannot penetrate deeply into the pores of cellulose fibres so the ratio is quite low. However, when we use a polymer with low molecular weight the ratio of charged polymer to cellulose is almost equal. I believe that some effects such as hydrophobicity and/or hydrogen bonding are very small.

**Dr. A. Alince, Páprican, Canada**

I wonder if the only driving force for the polymer adsorption is the charge as you suggest. When you adsorb the high molecular weight cationic polymer on cellulose and you compare the ratio of the charge on the polymer to the ratio of the accessible carboxyl groups on the cellulose, (the ones on the surface), you have something like 1,000:1 or 5,000:1 which gives you the impression that it is not really the main driving force. There were studies done where the adsorption capacity of the polyethyleneimine was studied as a function of the carboxyl group content of the cellulose, in which a good relationship was not established. The relationship was with the accessible surface. There was good agreement between the adsorption polymer and the accessibility of the surface.

**Miss H.G.M. van de Steeg, Wageningen Agricultural University, The Netherlands**

I have done a lot of experiments on the adsorption of cationic starch on microcrystalline cellulose and I think Mr. Marton agrees with me that the charge is really the important driving force for the adsorption. I have done experiments with different salt concentrations and it can be seen that the adsorption drops when the salt concentration increases. You also see that when you decrease the pH so that the charge on the surface gets lower then also the adsorbed amount drops. I think it is very clear that the charge has a lot to do with the adsorption.

**Dr. L. Odberg, STFI Sweden**

I would be extremely cautious in drawing any conclusions about availability based on experiments using polyimines because they have very broad molecular weight distributions. Therefore you can get any result you like if you choose a suitable equilibration

time, but maybe the studies you are talking about will define the materials used closely. I have seen no such studies - can you comment on this?

**Dr. B. Alince, Paprican, Canada**

We have done some studies working with polyethyleneimines which were reasonably monodisperse. These were low molecular weight and high molecular weight. I agree that the high molecular weight was difficult to describe in terms of its polydispersity. These were not BASF they were a different type of polyethyleneimine. But the fact is that the relationship between the accessible surface in the swollen pulp has a much better relationship to the amount of absorption capacity than you will find with carboxyl content. With the high molecular weight polymer, how many of the carboxyl groups are accessible to the polymer, which was very high molecular weight. What does the 5,000:1 ratio mean in terms of driving force? If you have 5,000 amino groups for every 1 carboxyl group. The polymer will adsorb very much in response to the pH because the polymer configuration of the polyethyleneimine is affected by pH. Therefore, the polymer configuration will determine the level of adsorption more than the carboxyl content.