Water-Soluble Polymers as Retention Aids in a Model Papermaking System. III. Modified Polyacrylamides

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Synopsis

The pigment retention efficiency, in a model papermaking system, of anionically and cationically modified polyacrylamides was compared to that of the unmodified homopolymer. The anionic polyacrylamide is a much less efficient retention aid, especially at high pH's; the nonionic and cationic polymers perform similarly and without any marked pH dependence. However, it is the nonionic and anionic polyacrylamides which are similarly poor at fiber flocculation, at pH's between 4.5 and 7.5, whereas the cationic polymer is a good fiber flocculant. All three polymers stabilize pigment suspensions. The anionic polymer is not effective in heteroflocculation of mixed dispersions of fibers and pigment, whereas both the nonionic and cationic are good flocculants, the latter being less susceptible to overdosing. Equilibrium adsorption isotherms were determined; the cationic polymer is, unlike the other modified polyacrylamide, very well adsorbed by cellulose fibers. Onto titanium dioxide, polymers adsorb in the order anionic<nonionic<cationic. A further differentiation of the cationic polymer is that it gives high pigment retention in sheet formation without markedly increasing the resistance to fluid flow through the forming sheet. Although a process of heteroflocculation is postulated for both nonionic and cationic polymers, in the former case it is thought that the primary adsorption is onto titanium dioxide, whereas with the latter it is onto cellulose.

INTRODUCTION

In the preceding two papers,[1,2] we describe the effects of two nonionic polymers, polyacrylamide and poly(vinylpyridine), on the retention of titanium dioxide particles in hand-made paper sheets. In order to establish the effect of copolymerized ionogenic groups, we now report on the retention behavior, and associated studies, of three commercial polyacrylamides, one of which is a homopolymer, one having some anionic repeat units, and the third some copolymerized cationic residues.

EXPERIMENTAL

The polymers were a gift from Allied Colloids Ltd., Bradford, England. Polymer N (Manufacturer's code Percol 351) is a high molecular weight homopolyacrylamide to which brief reference was made in an earlier paper.[1] Polymer

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A (Percol AN 139) contains some 5% (mole) acrylic acid units, whereas Polymer C (Percol CA 140) is reported to have 16.8% (mole) of an unspecified cationic comonomer. The measured contents of hydrolyzed acrylamide repeat units, found by titration with sodium hydroxide, are given in Table I, together with the conductivity of 0.10% aqueous solutions.

The reduced viscosity at 0.50% (w/v) concentration was measured over a range of pH values, these being adjusted by appropriate additions of HCl or NaOH (Fig. 1). The anionic polymer shows the viscosity behavior typical of a polyelectrolyte, but the supposed cationic polymer does not evidence the coil expansion which would be expected to result from ionization within the pH range studied.

Other experimental methods were as reported previously.[1]

RESULTS

Pigment Retention

The measurements made at pH 4.5 are illustrated in Figure 2. The anionic polyacrylamide, although capable of doubling the quantities of titanium dioxide retained in the paper sheet, is much less efficient than the nonionic and cationic samples, of which the latter is the better retention aid. On going to neutral (pH 6.5) conditions, the difference between polymer A and the others is more marked (Fig. 3). Although, on a relative basis, polymer A still doubles the retention value obtained in the absence of polymer, the absolute retention of ca. 25% is low. The cationic polymer remains slightly superior to the nonionic sample, and both exhibit a retention performance similar to that found in acid conditions. Addition of $10^{-5}M$ La(NO$_3$)$_3$ substantially increases the retention in a polymer-free system, but the added incorporation of polymer A only leads to additional retentions similar to those in salt-free conditions. On raising the pH to 8.0 (Fig. 4), the relative performance of the three polymers is unchanged.

Flocculation Studies

The effect on the colloidal stability of suspension of pulp fibers was studied, as before,[1] by the rate of subsidence of the flocs, the residual turbidity, and the volume of the sediment. The data are summarized in Table II.

Thus, in mildly acid solution, the anionic polymer slightly slows down the subsidence rate, removes a relatively small proportion of the suspended fiber fines, and gives a sediment of marginally greater volume. The nonionic poly-

TABLE I
Polymer Properties

Polymer	Hydrolyzed units, %	Specific conductivity,[a] (ohm^{-1} cm^{-1}) $\times$ 10^5
A	4.91	12.8
N	0.10	1.2
C	0.02	2.8

[a] In water.
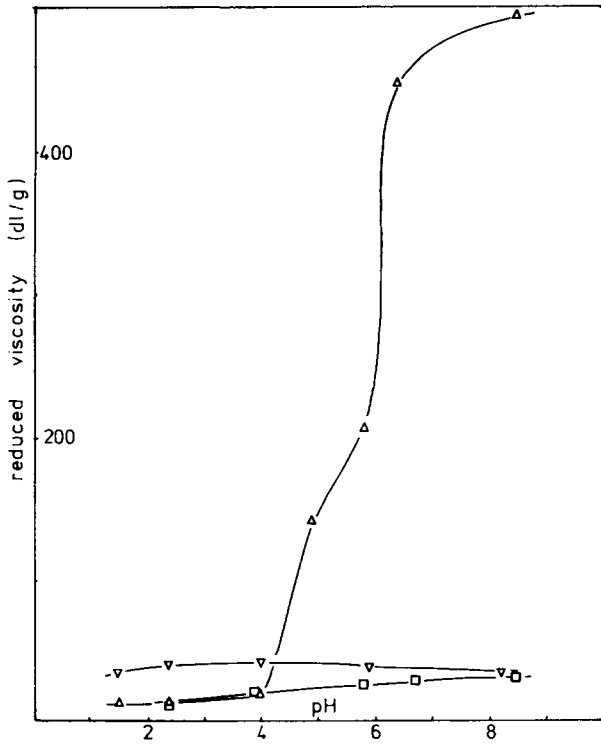
Fig. 1. Reduced viscosity (dl/g at 0.5% concentration) as function of pH: (▲) anionic polyacryl-amide (A); (▣) nonionic polyacrylamide (N); (▼) cationic polyacrylamide (C).
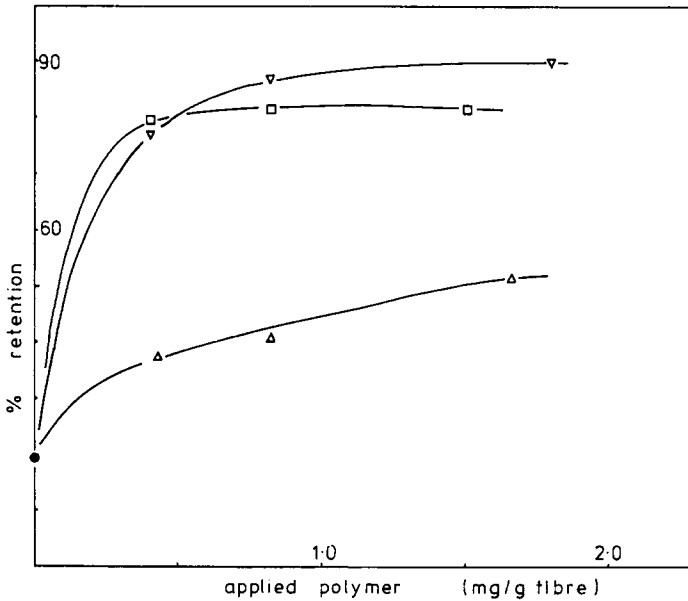

Fig. 2. Retention of titanium dioxide in hand-made sheets as function of amount of added polymer at pH 4.5. Symbols as in Fig. 1.
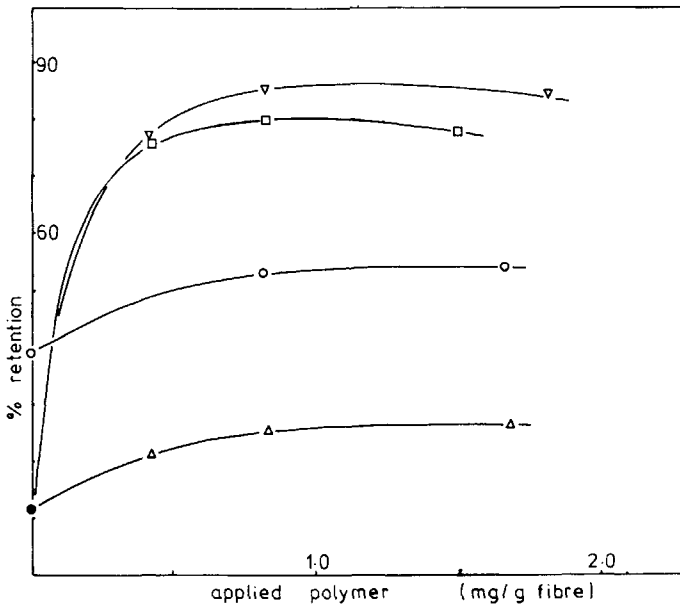
Fig. 3. Retention of titanium dioxide in hand-made sheets as function of amount of added polymer at pH 6.5. Symbols as in Fig. 1; (⊙) anionic polymer plus La^{3+} ions.

acrylamide, although slightly hastening the sedimentation, has only a small effect on supernatant clarity and has no effect on the sediment volume; its behavior is closely similar to that of sample PAM-5 reported earlier.[1] The cationic polymer, however, shows good flocculation behavior toward the fibers, noticeably
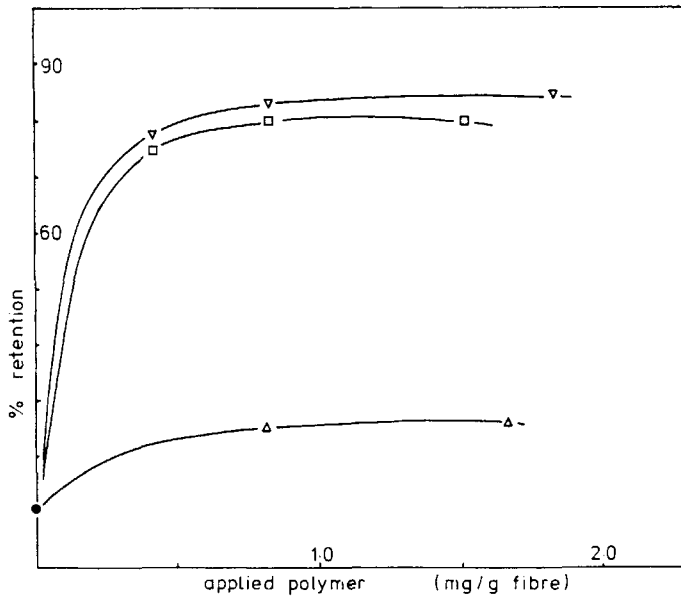

Fig. 4. Retention of titanium dioxide in hand-made sheets as function of amount of added polymer at pH 8.0. Symbols as in Fig. 1.

TABLE II
Fiber Flocculation by Modified Polyacrylamides (pH 4.5)

Applied polymer, mg/g fiber	Subsidence time, min			Optical density			Sediment volume, ml		
	A	N	C	A	N	C	A	N	C
0.000	26.0	26.0	26.0	0.224	0.224	0.224	129	129	129
0.375	28.0	—	16.2	0.222	—	0.098	135	—	137
0.750	—	—	14.8	—	—	0.078	—	—	143
0.875	30.1	—	—	0.204	—	—	137	—	—
1.250	—	21.2	—	—	0.191	—	—	130	—
1.500	—	—	11.0	—	—	0.050	—	—	137
2.000	30.5	—	—	0.194	—	—	138	—	—
2.500	—	21.3	—	—	0.188	—	—	129	—
3.000	31.2	—	—	0.178	—	—	139	—	—
3.375	—	—	10.4	—	—	0.024	—	—	145
3.750	—	19.1	—	—	0.191	—	—	126	—
4.125	—	—	13.4	—	—	0.022	—	—	140
5.125	—	—	18.4	—	—	0.024	—	—	146
5.500	31.6	—	—	0.174	—	—	138	—	—
6.125	—	—	—	—	—	0.015	—	—	145
7.500	—	20.0	—	—	0.200	—	—	128	—
11.000	32.6	—	—	0.180	—	—	141	—	—

speeding the subsidence rate, giving a relatively clear supernatant and a distinctly more voluminous sediment. The effects of the three polymers at pH 6.0 are summarized in Table III. Again, polymer A actually slows down the rate at which fibers fall out of suspension, has only a minor effect on supernatant clarity, and is without effect on the sediment volume. Polymer N is only marginally superior

TABLE III
Fiber Flocculation by Modified Polyacrylamides (pH 6.0)

Applied polymer, mg/g fiber	Subsidence time, min			Optical density			Sediment volume, ml		
	A	N	C	A	N	C	A	N	C
0.000	21.2	21.2	21.2	0.293	0.293	0.293	112	112	112
0.375	25.7	—	13.5	0.284	—	0.178	114	—	106
0.750	—	—	11.7	—	—	0.108	—	—	113
0.875	28.4	—	—	0.276	—	—	116	—	—
1.250	—	21.1	—	—	0.246	—	—	115	—
1.500	—	—	10.8	—	—	0.058	—	—	118
2.000	29.0	—	—	0.272	—	—	117	—	—
2.500	—	19.1	—	—	0.242	—	—	114	—
3.000	29.3	—	—	0.264	—	—	114	—	—
3.375	—	—	9.8	—	—	0.040	—	—	118
3.750	—	19.2	—	—	0.248	—	—	113	—
4.125	—	—	11.6	—	—	0.023	—	—	117
5.125	—	—	13.5	—	—	0.020	—	—	121
5.500	28.7	—	—	0.260	—	—	119	—	—
6.125	—	—	17.0	—	—	0.015	—	—	125
7.500	—	19.6	—	—	0.256	—	—	114	—
11.000	28.9	—	—	0.261	—	—	120	—	—

TABLE IV
Fiber Flocculation by Modified Polyacrylamides (pH 7.5)

Applied polymer, mg/g fiber	Subsidence time (min)			Optical density			Sediment volume (ml)		
	A	N	C	A	N	C	A	N	C
0.000	20.4	20.4	20.4	0.307	0.307	0.307	109	109	109
0.375	23.3	—	14.0	0.300	—	0.188	112	—	109
0.750	—	—	10.9	—	—	0.110	—	—	112
0.875	25.9	—	—	0.292	—	—	113	—	—
1.250	—	20.5	—	—	0.256	—	--	113	—
1.550	—	—	9.6	—	—	0.065	—	—	113
2.000	26.1	—	—	0.284	—	—	114	—	—
2.500	—	19.0	—	—	0.252	—	—	114	—
3.000	25.8	—	—	0.282	—	—	113	—	—
3.375	—	—	9.6	—	—	0.046	—	—	116
3.750	—	19.2	—	—	0.256	—	—	114	—
4.125	—	—	10.3	—	—	0.031	—	—	115
5.125	--·	—	12.6	—	—	0.016	—	—	121
5.550	27.1	—	—	0.276	—	—	113	—	—
6.125	—	—	14.1	—	—	0.015	—	—	117
7.500	—	19.2	—	—	0.272	—	—	113	—
11.000	27.4	—	—	0.275	—	·· —	112	—	—

to polymer A overall, but again the cationic polymer is outstandingly good at speeding sedimentation and bringing down fiber fines.

The results given in Table IV were obtained at a slightly alkaline pH and, in most respects, are similar to the data obtained at the lower pH's. Thus, polymers A and N, although showing slight differences in detail, are similar in general behavior, neither sample having any significant effect on the dispersion stability. Polymer C is again a good flocculant for the fibers. It is evident that, at all three pH values, polymer C shows the "overdosing" effect commonly observed with polymeric flocculants if judged by its effect on the subsidence rate of the fibers,

TABLE V
Effect of Modified Polyacrylamides on Dispersions of Titanium Dioxide

| Applied polymer, mg/l.	Optical density after 15 hr								
	pH 4.3			pH 6.0			pH 8.4		
	A	N	C	A	N	C	A	N	C
0	0.11	0.11	0.11	0.57	0.57	0.57	0.58	0.58	0.58
0.2	0.34	0.15	0.10	0.56	0.54	0.56	0.60	0.58	—
0.4	0.53	0.23	0.10	0.56	0.55	0.53	0.59	0.58	0.57
0.6	—	0.26	0.21	0.56	0.58	0.48	0.59	0.61	0.56
0.8	—	0.21	0.28	0.56	0.58	0.44	0.59	0.61	0.56
1.0	0.56	0.18	0.32	0.56	0.58	0.43	0.58	0.59	0.58
1.6	—	0.25	—	—	--	0.45	—	—	—
2.0	0.56	0.25	0.47	0.59	0.54	0.51	0.59	0.53	0.53
4.0	0.56	0.28	0.47	0.59	0.54	0.53	0.59	0.54	0.50
10.0	0.57	0.32	0.52	0.59	0.56	0.54	0.59	0.58	0.51
20.0	0.58	0.34	0.52	0.59	0.59	0.53	0.59	0.58	0.51
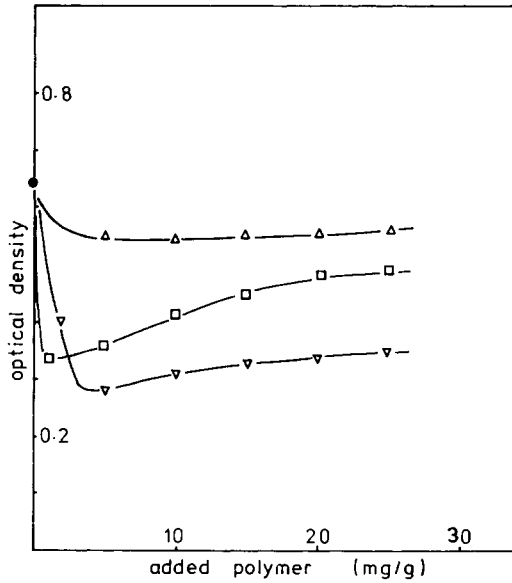
Fig. 5. Coflocculation of pigment and fibers as function of amount of added polymer at pH 4.3. Symbols as in Fig. 1.

but not if judged in terms of the supernatant clarity. That sediment volume proves to be a poor indicator of flocculation is, perhaps, not surprising for a system where the particles have high axial ratios.

Pigment dispersions were treated with polymer solutions as described previously.[1] The results are summarized in Table V. Suspensions of titanium dioxide at pH 4.3 are not very stable; and, at low polymer loadings, all the po-
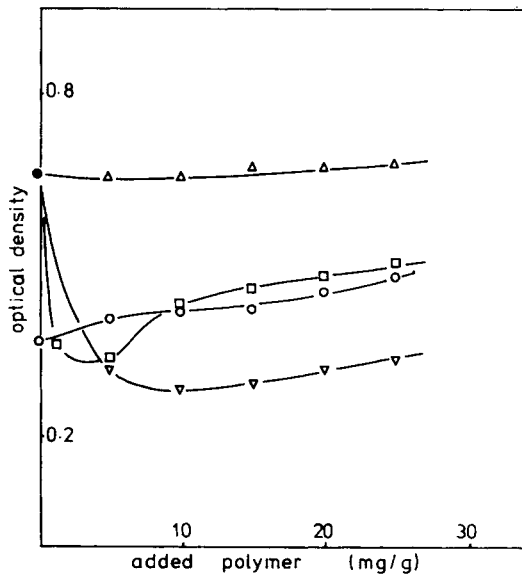
Fig. 6. Coflocculation of pigment and fibers as function of amount of added polymer at pH 6.2. Symbols as in Fig. 3.
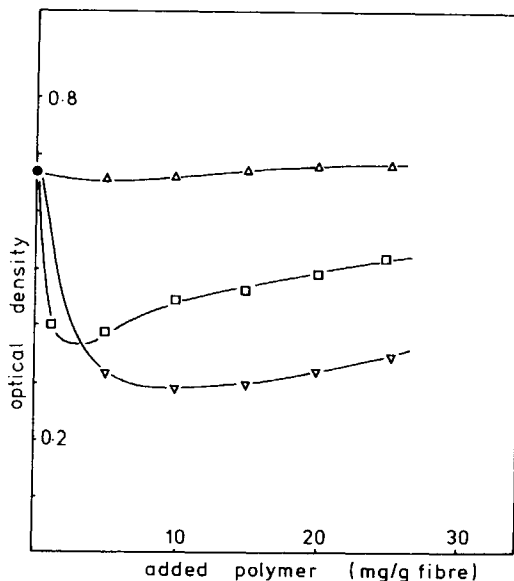
Fig. 7. Coflocculation of pigment and fibers as function of amount of added polymer at pH 7.9. Symbols as in Fig. 1.

lyacrylamides enhance dispersion stability, the anionic being more efficient than the nonionic which in turn is better than the cationic polymer. At high polymer loadings, both ionic polyacrylamides stabilize to a greater extend than the non-ionic sample. At the higher pH's, where the dispersion of titanium dioxide has relatively high natural stability, all three polymers are largely inert, the only noticeable effect being a slight flocculation by polymer C in neutral conditions

Coflocculation studies (10 parts fiber to 1 part pigment) were also made at
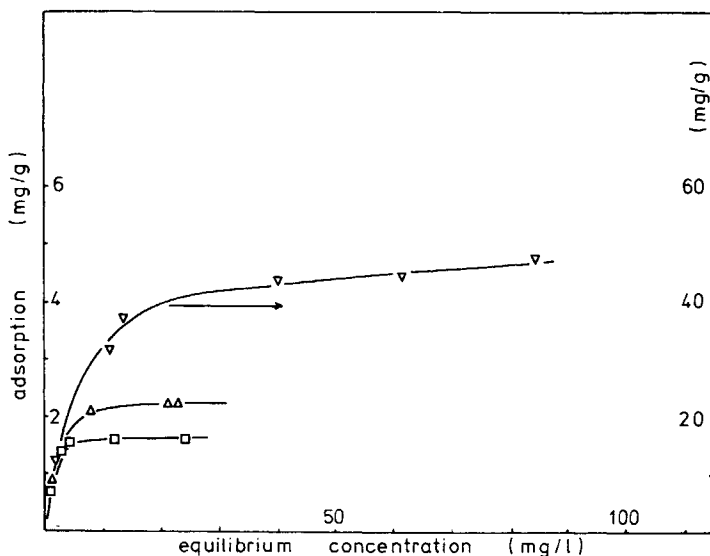
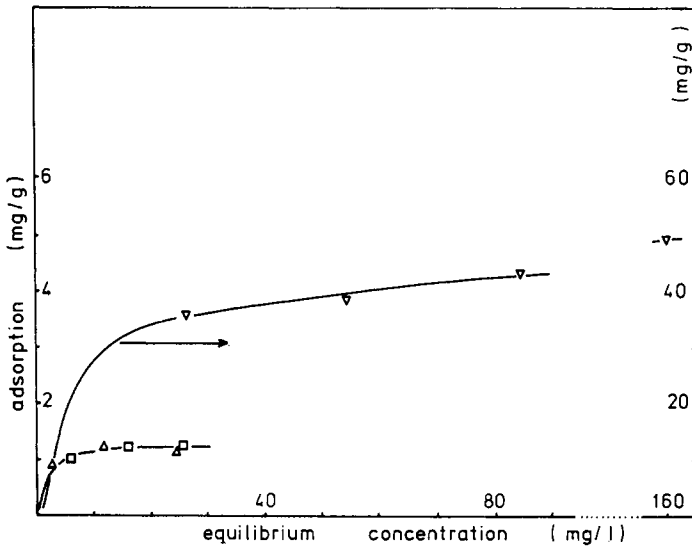
Fig. 8. Adsorption isotherms of modified polyacrylamides on fibers at pH 4.4. Symbols as in Fig. 1.
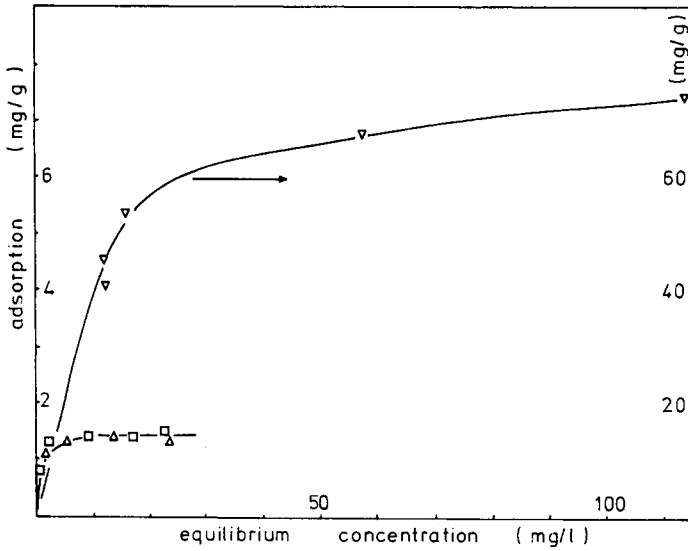
Fig. 9. Adsorption isotherms of modified polyacrylamides on fibers at pH 6.2. Symbols as in Fig.
1.

. three pH values. Figure 5 shows the behavior at pH 4.3. The degree of clarifi-
cation produced by polymer A is minor, whereas the other two polymers show
a marked effect. Polymer N has a marked effect at very low additions, but the
overdosing effect is quite severe, whereas polymer C shows less overdosing and
overall has the best heteroflocculation performance.

The coflocculation behavior is almost identical at pH 6.2 and pH 7.9 (Figs. 6
and 7). Thus, the anionic polymer is without effect; the nonionic polymer is good

Fig. 10. Adsorption isotherms of modified polyacrylamides on fibers at pH 7.6. Symbols as in
Fig. 1.
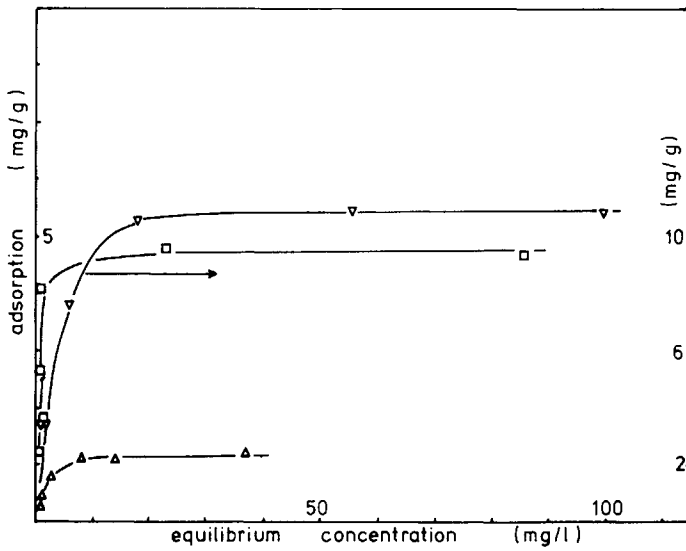
Fig. 11. Adsorption isotherms of modified polyacrylamides on titanium dioxide at pH 4.4. Symbols as in Fig. 1.

at very low additions, but some restabilization results at higher concentrations; whereas the cationic polymer, although requiring somewhat high concentrations, is almost free of overdosing. It is also interesting to note that the coagulation brought about by $10^{-5}M$ La^{3+} is not further enhanced by addition of polymer A.

Polymer Adsorption

Equilibrium adsorption isotherms were found for the modified polyacrylamides at three pH values onto both fibers and pigment. The concentration of
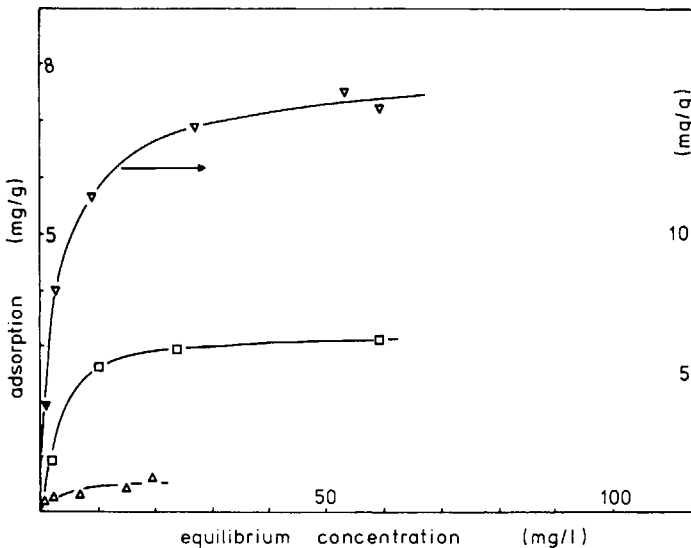
Fig. 12. Adsorption isotherms of modified polyacrylamides on titanium dioxide at pH 6.6. Symbols as in Fig. 1.
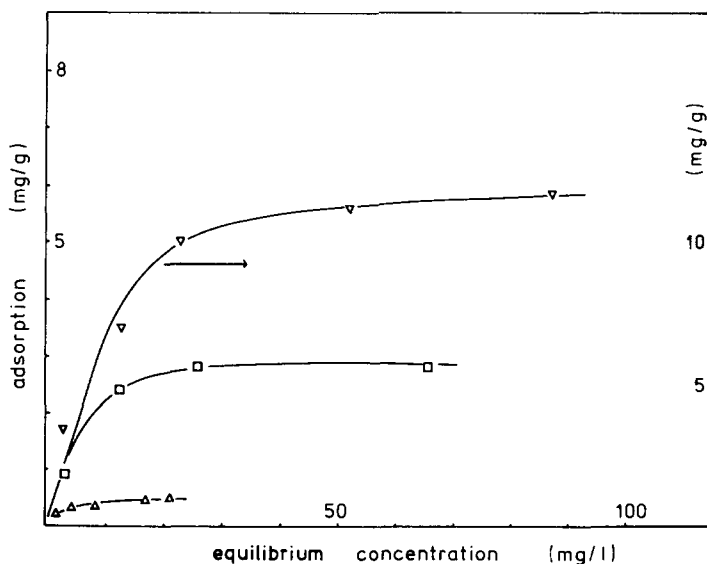
Fig. 13. Adsorption isotherms of modified polyacrylamides on titanium dioxide at pH 8.2. Symbols as in Fig. 1.

unadsorbed polymer was measured by the absorbance at 191.5 nm. Rate studies were made with polymer A at pH 6.0; the adsorption onto titanium dioxide had reached a constant value in less than 4 hr, but twice this time was needed for equilibrium adsorption onto fibers. Adsorption of polymers A and N onto fibers is low at all pH's (Figs. 8–10); ionization of the anionic polymer reduces its adsorption on to cellulose fibers at higher pH's, whereas the adsorption of the nonionic polymer is independent of pH. Earlier work in these laboratories[3] has shown that homopolyacrylic acid loses its adsorbability onto nylon above pH
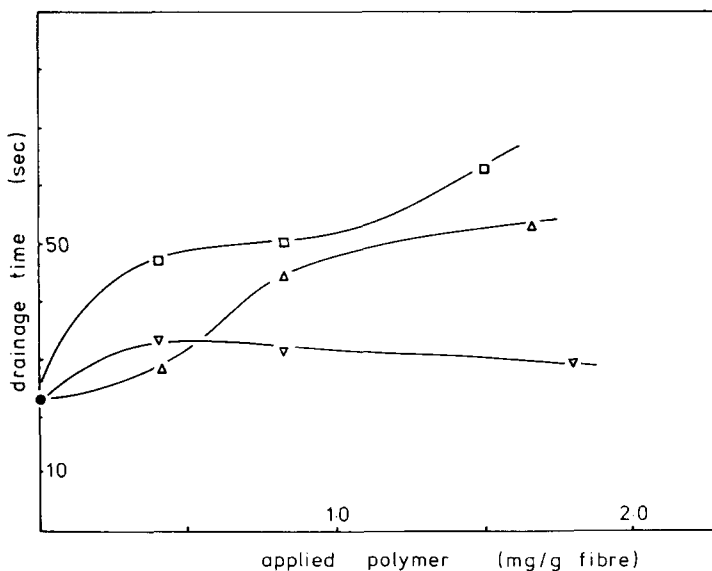
Fig. 14. Drainage time in sheet formation at pH 4.5 as formation of amount of added polymer. Symbols as in Fig. 1.
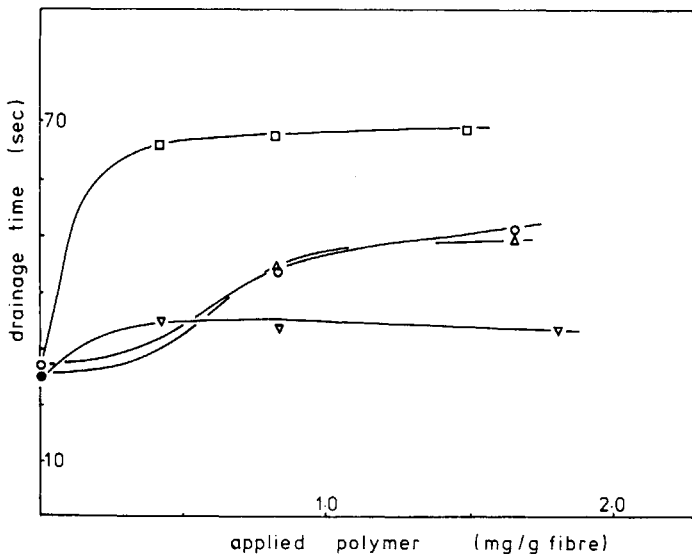
Fig. 15. Drainage time in sheet formation at pH 6.5 as function of amount of added polymer. Symbols as in Fig. 3.

6.0. More striking, however, is the high level of adsorption of the cationic polyacrylamide, more than an order of magnitude higher than the other samples and being greatest at neutral pH.

Adsorption onto the particles of titanium dioxide presents a rather similar picture (Figs. 11–13), but with more differentiation between samples A and N. The anionic polymer is hardly adsorbed, especially at higher pH's. The adsorption of the nonionic polymer drops somewhat with increase in pH, but is now some five times that of polymer A. The level of adsorption is rather less, however, than that of the laboratory-synthesized polyacrylamides reported earlier.[1] The high adsorption of the cationic polyacrylamide is again shown, although less so than onto cellulose; again the highest adsorption of polymer C is in neutral solution.

Drainage Times and Sheet Properties

At pH 4.5 (Fig. 14), both the anionic and the nonionic polyacrylamides increase the resistance to flow through the forming sheet, and both continue to increase the drainage time under conditions where the retention of titanium dioxide is leveling off. The cationic polymer, which is the best retention aid at pH 4.5, has remarkably little effect on the drainage time. Generally similar behavior is shown at pH 6.5 and pH 8.0 (Figs. 15 and 16). The nonionic polymer reaches a plateau of rather high drainage times which are somewhat greater than those found for the laboratory-made polyacrylamides,[1] whereas the cationic polymer behaves almost the same at all pH values examined. Addition of $10^{-5}M$ La^{3+} to systems containing polymer A at pH 6.5 has no effect on drainage through the sheet.

The relation between sheet opacity and retention of titanium dioxide takes the same form as in the preceding studies,[1,2] with no distinguishable pH trend.
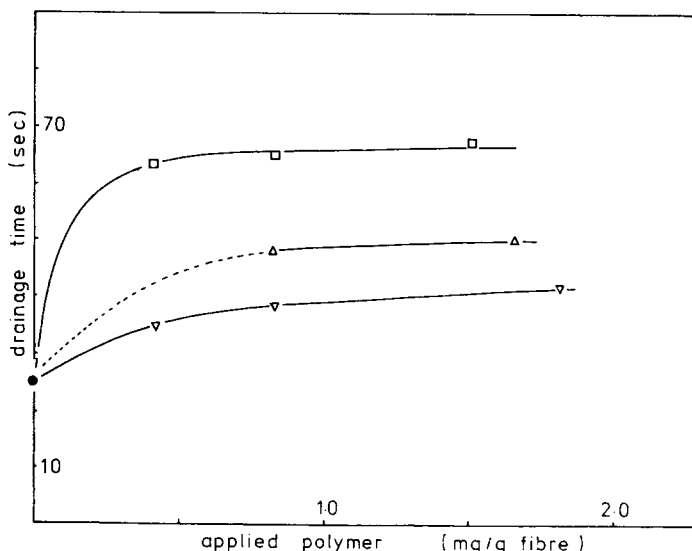
Fig. 16. Drainage times in sheet formation at pH 8.0 as function of amount of added polymer. Symbols as in Fig. 1.

It is noticeable, however, that, at a given pigment retention, polymer C consistently gives sheets of slightly higher opacities than does polymer N (Fig. 17), although the opacities are a little lower than those found with poly(vinylpyridines).[2]

DISCUSSION

There is one common feature in the behavior of the three polymers in the three pH regions: that is, the coflocculation measurements accurately mirror the pigment retention results. Combined with the previous observations[1,2] in this respect, we conclude that this simple measurement could adequately assess the pigment retention potential of candidate polymers.

The polyacrylamide which contains a small proportion of acrylic acid units (polymer A) is not a good retention aid in this model papermaking system. Such effects as this polymer shows are at low pH, where the acid groups are un-ionized. The equilibrium adsorptions are very low, though finite, and decrease as the polymer becomes charged. The resulting coil expansion, strikingly evidenced by the solution viscosity (Fig. 1), would greatly enhance bridging flocculation were it not that the repulsion between negatively charged polymer and solid surfaces prevents more than a tiny, and inadequate, adsorption.

At first examination, the nonionic and cationic polyacrylamides appear very similar in their retention performance, which is closely paralleled by the coflocculation data. Thus (Figs. 2–4) at all pH's polymer C slightly outperforms polymer N, a pattern repeated in coflocculation (Figs. 5–7) where the cationic polymer is seen to be less susceptible to "overdosing." The relative insensitivity of polymer C to pH suggests that the group copolymerized with acrylamide is not ionized within the range examined, a conclusion substantiated by the viscosity results (Fig. 1). Both polymers N and C stabilize dispersions of titanium
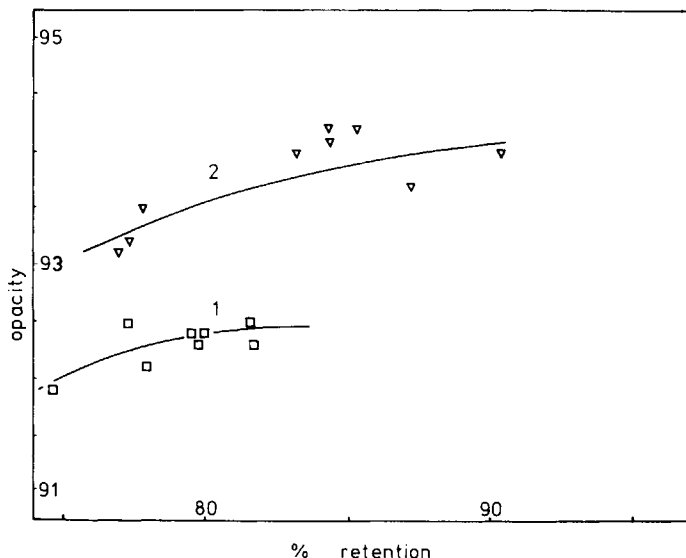
Fig. 17. Opacity (% contrast ratio) of dry sheet as function of retention of titanium dioxide in presence of modified polyacrylamides: (1) nonionic polymer N; (2) cationic polymer C.

dioxide and, again, both perform very similarly, although with some minor differences in detail. However, there are major differences in their behavior toward a fiber suspension. Whereas the nonionic polymer slightly destabilizes the dispersion, the cationic variant is an effective flocculating agent (Tables II–IV) at all pH's between 4.5 and 7.5. The equilibrium adsorption isotherms (Figs. 8–10) emphasize this distinction: at the isotherm plateau, the mass adsorption of polymer C on the fibers is 20–50 times that of polymer N. On the surface of titanium dioxide, however, the cationic polymer is adsorbed to a level some two to three times that of the nonionic polymer.

There are some dangers in extrapolating from equilibrium adsorption isotherms to the mechanism of sheet formation or even to the flocculation of mixed dispersions of titanium dioxide and cellulose fibers. First, the time scales are quite different, the isotherms being constructed after several hours of contact, the sheet being formed within a minute or so from first addition of polymer to dispersion. Secondly, in both retention and coflocculation studies, the polymer concentration is well below that at which the cationic polymer approaches its plateau adsorption. The adsorption isotherms are best regarded as indicating the relative propensity of the added polymer to interact with both fibers and pigment particles, and there is no doubt that the cationic comonomer units in polymer C do lead to enhanced surface attachment. High equilibrium adsorptions are, however, clearly not a requirement for good retention performance, and the poly(vinylpyridines) reported earlier,[2] for instance, have modest adsorptions on both surfaces but are good at retaining pigment in the paper sheet.

That the mechanism of the process is somewhat different between polymer N and C is clearly indicated by the drainage time in sheet formation. The cationic polymer, at all three pH levels, only slightly slows down the transport of water through the forming sheet although trapping the particles of titanium dioxide very efficiently. The nonionic polymer, on the other hand, exhibits its

good retention at the expense of more than doubling the drainage time. It is tempting to envisage the following processes. The cationic polymer preferentially adsorbs onto fibers to give open aggregates which entrap pigment particles and bind them by the bridging action of the polymer: the forming sheet will be relatively free draining and the pigment relatively unagglomerated. The nonionic polymer tends to adsorb more on titanium dioxide to give larger pigment aggregates, which then bind to the fibers as polymer adsorption proceeds. This balance of adsorption between fibers and pigment is in accord with the coflocculation data of Figures 5–7; the nonionic polymer reduces the supernatant turbidity, which is predominately a measure of suspended pigment, markedly at very low additions and more so than does the cationic polymer, but also restabilizes the dispersion at higher loadings. Further, the sheet opacities, at a given total pigment content of the sheet, are higher when the cationic polymer is used, which is also consistent with the above description. A limited number of scanning electron micrographs were taken of paper sheets, but it was not possible to obtain unambiguous visual evidence to substantiate the supposed different degrees of agglomeration with polymers N and C.

References

1. G. J. Howard, F. Lyth Hudson, and J. West, *J. Appl. Polym. Sci.*, **21**, 1 (1977).
2. G. J. Howard, F. Lyth Hudson, and J. West, *J. Appl. Polym. Sci.*, **21**, 17 (1977).
3. D. Cole and G. J. Howard, *J. Polym. Sci. A-2*, **10**, 993 (1972).