

## Water-Soluble Polymers as Retention aids in a Model Papermaking System. IV. Some Block and Graft Copolymers

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### Synopsis

In an attempt to relate the retention behavior of water-soluble polymers in paper formation from cellulose fibers and titanium dioxide, several copolymer types were synthesized. These were acrylamide-acrylonitrile random copolymers; block copolymers of acrylamide, acrylonitrile, and 2-vinylpyridine with poly(ethylene oxide); and acrylamide graft copolymers of ethyl hydroxyethyl cellulose. Good retention and heteroflocculation behavior is shown only by the first of the above types of copolymers. Generally speaking, block copolymeric structures synthesized were of molecular size too small to act as good retention aids, although in a number of cases their performance was noticeably superior to that of the homopolymer analog. Adsorption isotherms are also reported and the overall results discussed in terms of a polymer bridging mechanism of heteroflocculation.

### INTRODUCTION

The preceding papers<sup>1-3</sup> have shown how the retention of titanium dioxide pigment in a sheet of cellulose fibers may be substantially increased by the addition of suitable, high molecular weight, water-soluble polymers and how this effect is largely a consequence of a heteroflocculation. A bridging flocculation of two particles by a polymer molecule would be expected to be particularly efficient if its structure contained adsorbable "anchor" segments well separated by nonadsorbable, well-expanded chain sequences; graft and ABA block copolymers are indicated, as was pointed out in the context of mineral processing by Slater, Clark, and Kitchener.<sup>4</sup> We report some studies of retention in a model papermaking system by copolymers of various structures so that the results may be compared to those obtained with homopolymers and randomly modified homopolymers.

### EXPERIMENTAL

#### Polymer Syntheses and Characterization

**Acrylamide/Acrylonitrile Random Copolymer.** First, some random copolymers of acrylamide and acrylonitrile were prepared by a procedure generally

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TABLE I  
 Acrylamide-Acrylonitrile Copolymers

Code	[Initiator]/[monomer] <sup>a</sup>	$\eta_{sp}/c$ , <sup>b</sup> dl/g	Acrylonitrile content, mole fraction
PAMAN-1	$2.0 \times 10^{-6}$	9.66	0.141
PAMAN-2	$4.6 \times 10^{-7}$	30.9	0.138
PAMAN-3	$2.8 \times 10^{-7}$	111.8	0.129

<sup>a</sup> Molar ratio of equimolar persulfate and bisulfate to mixed monomers.

<sup>b</sup> At 0.5% (w/v) in water at 25°C.

similar to that employed for acrylamide homopolymerization; the acrylonitrile was treated with sodium hydroxide, dried, and fractionally distilled before use. Reduced viscosities of 0.5% (w/v) aqueous solutions were measured at 25°C (Table I). The acrylonitrile content of the copolymers was estimated from the infrared spectrum (KBr disk) by measuring the peak height ratio for the CN absorption at  $2260 \text{ cm}^{-1}$  and the CH ( $2920 \text{ cm}^{-1}$ ) band and comparing the result to a calibration established from mixtures of acrylonitrile and acrylamide homopolymers. The reduced viscosities are very similar to those of polyacrylamides synthesized with corresponding initiator contents.<sup>1</sup> These copolymers are water soluble, but polymers of higher acrylonitrile content are only partially water soluble.

**Ethylene Oxide Block Copolymers by Radical Mechanism.** Some attempts to form high molecular weight block copolymers on a performed poly(ethylene oxide) were made. High molecular weight polymers of approximate molecular weights  $4.0 \times 10^4$ ,  $6.0 \times 10^5$ ,  $4.0 \times 10^6$ , and  $5.0 \times 10^6$  (Polyox, Union Carbide Ltd.) were used. Novitskaya and Konkin<sup>5</sup> initiated acrylonitrile polymerization on the hydroxyl ends of a low molecular weight poly(ethylene oxide) by the ceric ion technique, and we have attempted similar block copolymerizations with the high molecular weight poly(ethylene oxides). However, initial experiments showed the viscosity of a reaction mixture containing Polyox and ceric ion at acid pH decreased rapidly to about one-third of its original value, whether or not monomer was also present. After some 20 min, the exact time depending on reactant concentrations, the viscosity-time curve flattened out, even in the presence of monomer.

A typical reaction was conducted as follows: To 50 ml of a 1% solution of high molecular weight poly(ethylene oxide) in distilled water were added 2 g recrystallized acrylamide. After the monomer had gone into solution, 10 ml acidified ammonium ceric sulfate were added (ceric ion,  $1 \times 10^{-3}M$ , hydrogen ion,  $2 \times 10^{-3}M$ ). The reaction was terminated after 1 hr and the product precipitated by addition of a acetone/diethyl ether mixture and dried *in vacuo*. The reduced viscosity in water was approximately one-third that of the original poly(ethylene oxide). The reaction period of 1 hr was chosen since, in the absence of poly(ethylene oxide), homopolyacrylamide did not start to form until after an induction period of this magnitude.

When acrylonitrile was substituted for acrylamide, the same viscosity decrease was observed. However, after some 20 min of reaction, the system became turbid and polymer precipitated. This was taken to be an ethylene oxide-acrylonitrile block copolymer since the water-washed product had an infrared spectrum exhibiting both nitrile and ether absorptions and was insoluble in conditions where

TABLE II  
Ethylene Oxide–Acrylonitrile Block Copolymers

Code	PEO, g	Acrylonitrile, g	Reduced viscosity (PEO), dl/g <sup>a</sup>	N, %	Reduced viscosity (product), dl/g <sup>a</sup>
PAN-PEO-1	2.5	1.63	0.17	3.9	— <sup>b</sup>
PAN-PEO-2	5.0	8.07	6.93	0.1	6.42
PAN-PEO-3	2.0	16.1	71.4	0.2	63.1
PAN-PEO-4	1.0	8.07	99.3	0.2	75.7

<sup>a</sup> At 0.5% concentration 25°C.

<sup>b</sup> Not soluble.

poly(ethylene oxide) is dissolved (e.g., xylene at 45–50°C). A number of variants on the general procedure were made in an attempt to reduce the poly(ethylene oxide) scission and increase the product solubility.

**Ethylene Oxide Block Copolymers by Ionic Mechanism.** An alternative method of using the hydroxyl ends of poly(ethylene oxides) to initiate block copolymerization is that of Furukawa et al.<sup>6</sup> The polymer was reacted with sodium and the alcoholate so formed used to initiate anionic polymerization. Well-dried poly(ethylene oxide) (1 g) was dissolved in dry xylene (150 ml) at 45–55°C, small pieces of sodium metal (0.2 g) were added, and then the mixture was refluxed under nitrogen for 6 hr. After cooling to 40°C, the solution was decanted from the sodium and 10 ml purified acrylonitrile added with stirring. After standing overnight under nitrogen, a product was precipitated which was washed with ether and dried *in vacuo*. Aqueous solutions were slightly turbid, and the product from the lowest molecular weight poly(ethylene oxide) was only partially water soluble (Table II).

Attempts were also made to initiate 2-vinylpyridine polymerization at the ends of poly(ethylene oxide) chains by the anionic reaction described above. The product which was based on PEO-3 was well washed with methanol before characterization. The content of poly(2-vinylpyridine) was estimated at 0.42% by comparison of the 262-nm absorption of a solution in dilute hydrochloric acid (pH 4) to a calibration derived from homopoly(2-vinylpyridine) solutions. The reduced viscosity of an 0.5% solution (pH 4) was 70.3 dl/g, only slightly less than that of the parent poly(ethylene oxide). A final modification to a poly(ethylene oxide) was to react a xylene solution at 60° with excess stearoyl chloride so as

TABLE III  
Ethylhydroxyethyl Cellulose–Acrylamide Graft Copolymers

Code	EHEC, g	Acrylamide, g	Reduced viscosity (EHEC), dl/g <sup>a</sup>	N, %	Reduced viscosity (product), dl/g <sup>a</sup>
EHEC-1-PAM-1	1.0	1.0	24.2	0.1	21.5
EHEC-1-PAM-2	1.0	2.0	24.2	2.4	11.1
EHEC-1-PAM-3	1.0	2.0	24.2	2.1	6.9
EHEC-2-PAM-4	1.0	2.0	33.8	2.5	7.9

<sup>a</sup> At 0.5% concentration 25°C.

to end-cap the polymer with hydrophobic groups. The reduced viscosity of this product was 68.9 dl/g.

**Acrylamide Graft Copolymers.** Some acrylamide graft copolymers were synthesized onto ethylhydroxyethyl cellulose (Modocolls EK600 and ED1200, Mo och Domsjö A.B., Sweden) by the ceric ion method as described earlier. Again, the reduced viscosity of the product was well below that of the parent ethylhydroxyethyl cellulose (Table III).

### Methods

Other experimental methods were as reported previously.<sup>1</sup> The supernatant concentrations of poly(ethylene oxide), ethylhydroxyethyl cellulose, and their derived copolymers were determined gravimetrically; reproducibilities in adsorption estimation, onto both fibers and pigment, were within 5%.

## RESULTS

### Coflocculation

The studies made on other polymers in the model papermaking system<sup>1-3</sup> all showed how the coflocculation test mirrored the pigment retention in sheet formation. The coflocculation test was, therefore, used as a primary rating for the polymers made as described above. The following polymers had no coflocculation ability: poly(ethylene oxide) and its derivatives with acrylamide and

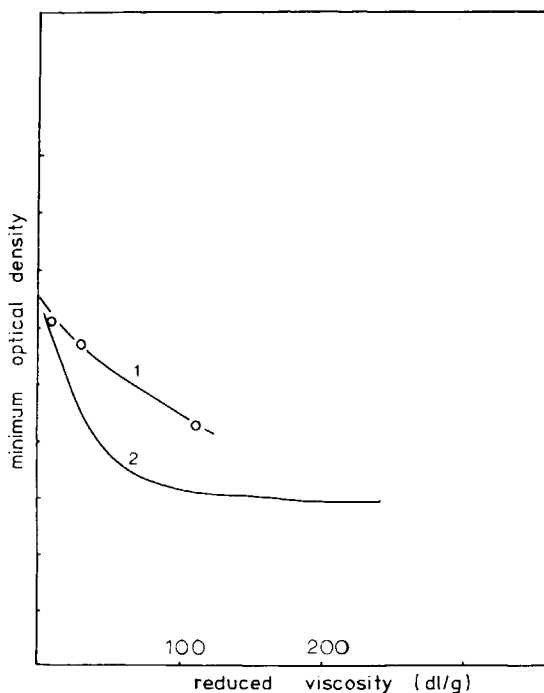


Fig. 1. Minimum optical density in coflocculation test at pH 6.5 as function of reduced viscosity: (1) PAMAN copolymers; (2) polyacrylamide homopolymers.

acrylonitrile as made by the ceric ion technique. Of the acrylonitrile and vinylpyridine block copolymers based on poly(ethylene oxide), one product only, P2VP-PEO-3, showed strong coflocculation behavior. This was at pH 4, but large additions of polymer, relative to vinylpyridine homopolymers, were necessary. Ethylhydroxyethyl celluloses and their derivatives were also without coflocculating abilities, with the exception of EHEC-2-PAM-4, which had a slight effect at pH 6.5. The random copolymers of acrylamide and acrylonitrile are, however, good coflocculants of mixed pigment/fiber dispersions although less efficient than homopolyacrylamides of similarly reduced viscosity. The general shape of the coflocculation curves are as with homopolymers (e.g., Fig. 2 of ref. 1,) and Figure 1 shows how the minimum optical density varies with the molecular size of the copolymer, the polyacrylamide data being given as reference.

### Retention

A number of retention determinations were made, including some with polymers which, on the coflocculation test, would be expected to be inactive. Figure 2 summarizes some of these data obtained at pH 6.5. Even very high molecular weight poly(ethylene oxides) have an almost negligible effect on the pigment retention. Two modified poly(ethylene oxides) were also examined: although their retention efficiency is very low, it is noticeable that incorporation of end segments, either stearyl or poly(vinylpyridine), do improve the performance over that of the parent polymer.

Neither sample of ethylhydroxyethyl cellulose increases the pigment retention: two acrylamide-grafted copolymers do, however, show a minor enhancement of retention, and the data are tabulated in Table IV. These minor improvements in pigment retention during sheet formation are shown by polymer structures which gave little or no evidence of an ability for heteroflocculation; the correlation

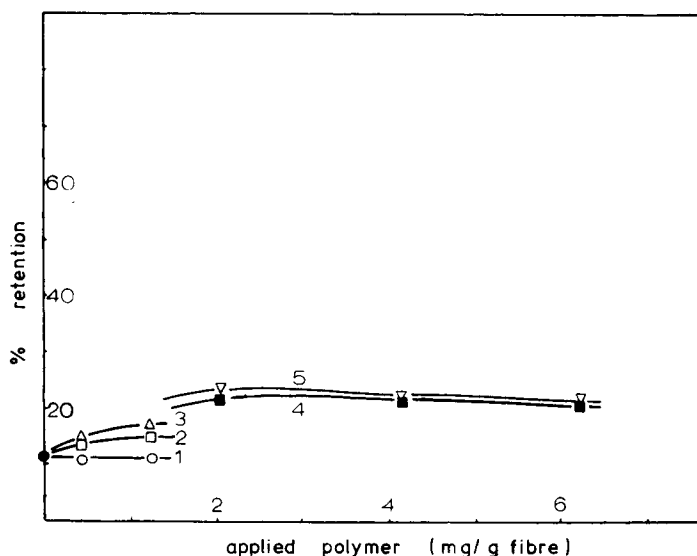


Fig. 2. Retention of titanium dioxide in sheet formation at pH 6.5: (1) PEO-2; (2) PEO-3; (3) PEO-4; (4) P2VP-PEO-3; (5) PEO-3-stearyl.

TABLE IV  
Retention of Titanium Dioxide by Ethylhydroxyethyl  
Cellulose-Acrylamide Graft Copolymers

Code	Applied polymer, mg/g	Retention, %	
		pH 4.3	pH 6.5
—	0	19.8	11.9
EHEC-1-PAM-2	2.08	—	29.2
EHEC-1-PAM-2	4.17	30.6	29.2
EHEC-1-PAM-2	6.25	31.4	28.7
EHEC-2-PAM-4	2.07	30.9	30.3
EHEC-2-PAM-4	6.25	31.1	30.7

previously noted between the coflocculation test and the retention performance seems reliable only at higher levels of retention.

The most significant improvements in pigment retention by the copolymers synthesized in this study are shown by the acrylamide-acrylonitrile random copolymers (Fig. 3). The retention performance of these three copolymers is very similar to that of polyacrylamide homopolymers of similar reduced viscosities (see Fig. 1 of ref. 1).

### Adsorption

Equilibrium adsorption isotherms were determined for several of the copolymers. Onto fibers, the highest molecular weight poly(ethylene oxide) was only adsorbed to a very slight extent, not exceeding 0.1 mg/g. However, the block polymer P2VP-PEO-3 shows a finite absorption at pH 6.4 (Fig. 4), but with an unusual, almost linear, isotherm. Homopoly(vinylpyridines)<sup>2</sup> show a substantial adsorption onto cellulose fibers but with a normal Langmuir-type isotherm. Random copolymers show slight adsorption, as do homopolyacrylamides.<sup>1</sup> The

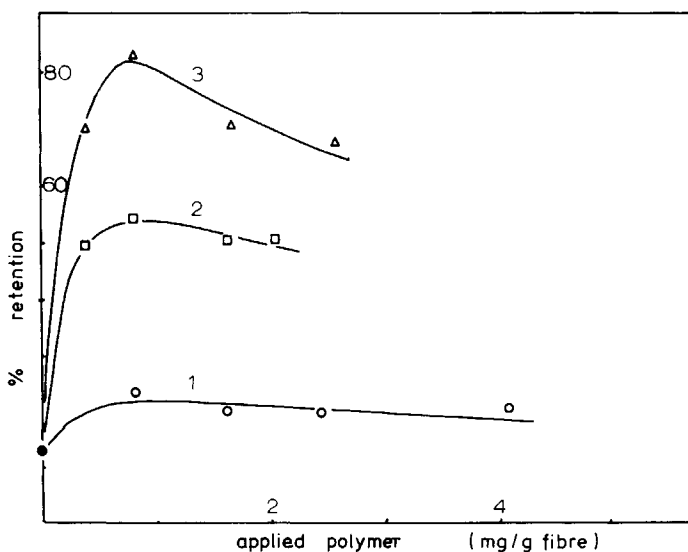


Fig. 3. Retention of titanium dioxide in sheet formation at pH 6.5: (1) PAMAN-1; (2) PAMAN-2; (3) PAMAN-3.

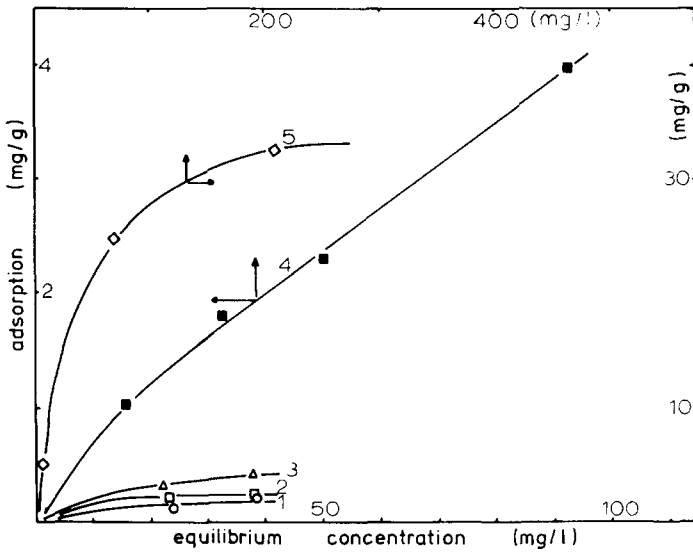


Fig. 4. Equilibrium adsorption isotherm on fibers at pH at 6.5: (1) PAMAN-1; (2) PAMAN-2; (3) PAMAN-3; (4) P2VP-PEO-3; (5) EHEC-2.

ethylhydroxyethyl cellulose is extremely well adsorbed on fibers (Fig. 4), and we presume that the acrylamide-grafted derivatives will be similarly well adsorbed.

Poly(ethylene oxides) are only slightly adsorbed, to less than 0.1 mg/g, by titanium dioxide. The block copolymer of ethylene oxide and vinylpyridine is adsorbed, again with a Henry's law type of isotherm (Fig. 5). The adsorption isotherms of the PAMAN copolymers are similar to those of the polyacrylamides

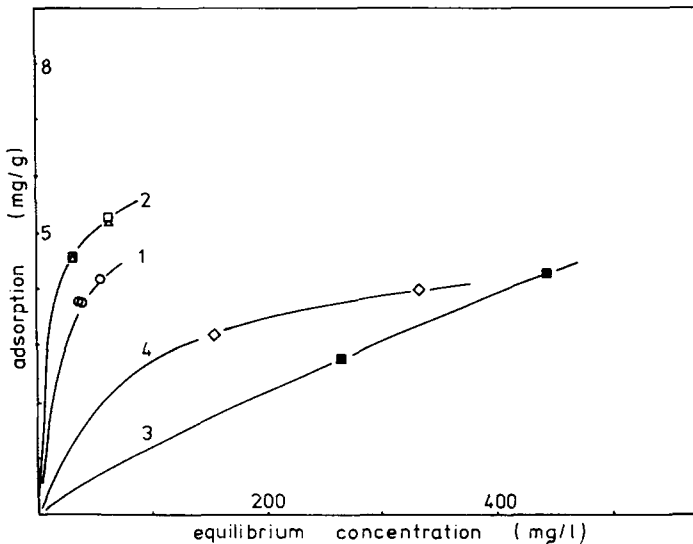


Fig. 5. Equilibrium adsorption isotherms on titanium dioxide at pH 6.5: (1) PAMAN-1; (2) PAMAN-2 and PAMAN-3; (3) P2VP-PEO-3; (4) EHEC-2.

TABLE V  
Drainage Time in Sheet Formation

Code	Applied polymer, mg/g	Drainage time, sec		Opacity, %	
		pH 4.3	pH 6.5	pH 4.3	pH 6.5
—	0	23.4	24.8	77.9	76.3
EHEC-1-PAM-2	2.08	—	32.6	—	84.9
EHEC-1-PAM-2	4.17	31.0	34.0	—	86.2
EHEC-1-PAM-2	6.25	31.4	33.7	—	84.9
EHEC-2-PAM-4	2.07	32.9	33.1	85.8	85.7
EHEC-2-PAM-4	6.25	33.2	33.8	86.1	85.9
PEO-3-Stearoyl	2.06	—	28.7	—	—
PEO-3-Stearoyl	4.17	—	29.0	—	—
PEO-3-Stearoyl	6.23	—	29.0	—	—
P2VP-PEO-3	2.06	—	28.8	—	82.1
P2VP-PEO-3	4.18	—	29.4	—	81.9
P2VP-PEO-3	6.21	—	29.2	—	82.3
PAMAN-1	0.82	—	26.5	—	81.1
PAMAN-1	1.63	—	27.1	—	80.9
PAMAN-1	2.46	—	28.3	—	80.6
PAMAN-1	4.11	—	28.1	—	80.7
PAMAN-2	0.41	—	32.2	—	88.9
PAMAN-2	0.82	—	36.8	—	89.2
PAMAN-2	1.64	—	40.5	—	88.9
PAMAN-2	2.06	—	40.2	—	88.5
PAMAN-3	0.42	—	36.1	—	91.9
PAMAN-3	0.83	—	42.3	—	92.4
PAMAN-3	1.67	—	47.3	—	91.8
PAMAN-3	2.60	—	51.6	—	91.2

reported earlier,<sup>1</sup> while the ethylhydroxyethyl cellulose exhibits a modest adsorption level onto titanium dioxide.

### Drainage During Sheet Formation

The PAMAN copolymers, which gave the best retention results, are also similar to polyacrylamide homopolymers in their drainage behavior. Thus, an increased retention efficiency is accompanied by a slower sheet formation; and whereas the pigment retention tends to an optimum value at a critical range of polymer loading, the drainage time increases monotonically (Fig. 6). Drainage times for other polymers studied for their retention effect are tabulated in Table V.

## DISCUSSION

It is clear that, as an exercise to illustrate the supposed superiority of block and graft copolymers as flocculants, the work reported here is somewhat of a failure. Nonetheless, a number of conclusions can be drawn which fit in with the general picture of polymer-assisted pigment retention established in the preceding papers.<sup>1-3</sup> First, the coflocculation test is a fair, but not perfect, mirror of retention in sheet formation. Thus, some polymers judged to be quite ineffective by the test do have a slight effect on retention. The system giving the best results, the acrylamide-acrylonitrile random copolymers, is not as highly



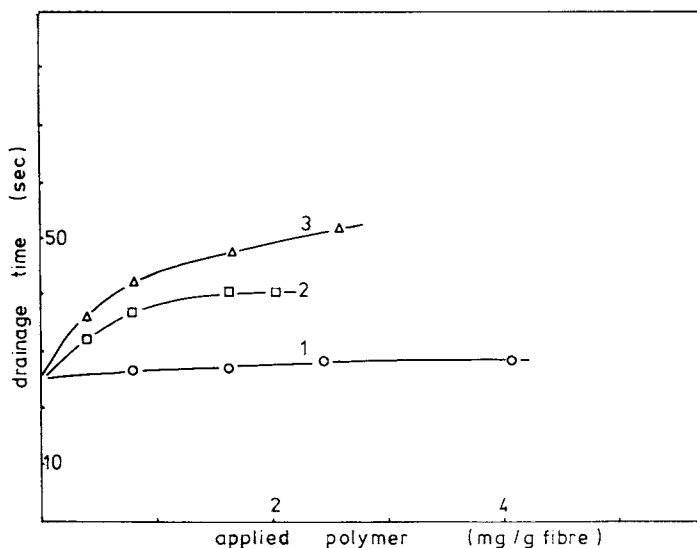


Fig. 6. Drainage time in sheet formation at pH 6.5 as function of amount of added polymer: (1) PAMAN-1; (2) PAMAN-2; (3) PAMAN-3.

rated as the corresponding homopolyacrylamides by coflocculation. However, in retention (together with drainage time and sheet opacity), their performance is very similar to a homopolymer of like coil size.

The failure of some of the block polymers to exhibit any retention or flocculation effect must be attributed to an insufficient molecular size in solution consequent on unavoidable chain scission during their syntheses. High molecular weight alone is not enough; thus, the poly(ethylene oxides), although of very high degree of polymerization, barely contribute any additional pigment retention, since they have no appreciable adsorption onto either pigment or cellulose. However, putting stearyl or poly(vinylpyridine) end-caps onto the poly(ethylene oxide) improved the retention, although to an extent well below that needed in industrial practice, and, in the former example, at least, substantially increased the adsorbability.

Conversely, high adsorption is not sufficient to ensure an effective retention of pigment in sheet formation. The ethylhydroxyethyl celluloses are highly adsorbed by fibers and sufficiently well by pigment, but they are quite without effect on retention; this may represent the consequence of insufficient molecular size of these rather inflexible chains. However, it is difficult to see why acrylamide-grafted derivatives in which some main chain scission has occurred and which have noticeably smaller solution viscosities do, nonetheless, have a small but significant retention effect. All the polymers reported in this paper which increase pigment retention do so at the expense of increasing the time required for sheet formation. Indeed, of all the polymer types studied in this program,<sup>1-3</sup> only the cationic systems, the poly(vinylpyridine) homopolymers and the cationic derivative of polyacrylamide, have the ability to give very high pigment retention with little increase in the drainage time.

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