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P. Lepoutre^a; S. H. Hui^a; A. A. Robertson^a

^a Pulp and Paper Research Institute of Canada Pointe Claire, Quebec, Canada

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Some Properties of Polyelectrolyte-Grafted Cellulose

P. LEPOUTRE, S. H. HUI, and A. A. ROBERTSON

Pulp and Paper Research Institute of Canada
Pointe Claire, Quebec, Canada H9R 3J9

ABSTRACT

Anionic and cationic polyelectrolytes were grafted on a bleached kraft pulp. Grafting an anionic polyelectrolyte (sodium polyacrylate-polyacrylamide copolymer) resulted in modified fibers possessing outstanding affinity for water and saline solutions in the pH range where the polymer is ionized. Swelling is the result of both the grafting operation itself and of the presence of the ionized polyelectrolyte.

The swollen grafted fibers could be disintegrated under intense shear to give a colloidal solution exhibiting pseudoplastic thixotropic behavior. Electron microscopic examination revealed that during the shearing process the fiber had been disintegrated into its constitutive elements, long rodlike protofibrils, which are believed to be mainly responsible for the high viscosities observed.

Grafting a cationic polyelectrolyte (polydimethylamino ethyl methacrylate hydrochloride) produced fibers with lower but significant water swelling. The influence of pH on swelling was similar, although reversed, to that observed with the anionic grafted fibers. The presence of a large number of cationic groups in the porous cellulose fiber gel points to applications in ion-exchange and adsorption processes.

INTRODUCTION

Many attempts have been made to modify pulp and paper by graft copolymerization [1], and these studies have generally had as their objective the improvement of the properties of a sheet of paper, be it tensile strength, tear, or dimensional stability. Less has been done on the modification of pulp fibers for applications other than paper.

In recent years there has been a growing demand for pulp in the sanitary products area where liquid absorbency is very important, and several cellulosic products with high water absorbency have been developed. Such products are usually substituted celluloses in fibrous form [2, 3]. This paper reviews some of the recent work done in our laboratories on the modification of pulp fibers by graft polymerization of polyelectrolytes, both anionic and cationic, to confer on them improved liquid absorbency. It also describes some of the properties of the colloidal solutions which can be obtained from these highly swollen fibers.

ANIONIC POLYELECTROLYTE GRAFTS

Liquid Absorbency

The approach taken to prepare the anionic grafts was that used by Adams and Hoftieser [4] and by Gugliemelli et al. [5] who worked with starch. Acrylonitrile is grafted first and then the nitrile groups are hydrolyzed, under alkaline conditions, into amide and carboxylate groups resulting in a copolymer of approximately 60% sodium polyacrylate and 40% polyacrylamide. A never-dried bleached softwood pulp was used and grafting was done by the ceric ion process. More details on the preparation and characterization of these copolymers may be found in Ref. 6.

The hydrolyzed polyacrylonitrile grafted fibers exhibit considerable swelling in water as shown in Fig. 1. Not only are the modified fibers very swollen but they hold the water tenaciously. Figure 2 shows the amount of water retained after centrifugation under $900 \times$ gravity for 30 min, expressed as water retention value (WRV) in g H₂O per g fiber, versus graft level expressed as PAN. Also shown in Fig. 2 is the saline retention value, SRV, obtained in a similar way, but using 1% aqueous NaCl instead of distilled water. (1% aqueous NaCl is used to simulate the physiological fluids for which this type of product is designed.)

It is seen here that both water and saline retention values increased rapidly with graft level and then leveled off at 30 to 40 g/g as the graft level reached 120 to 140%. These WRV levels have been confirmed

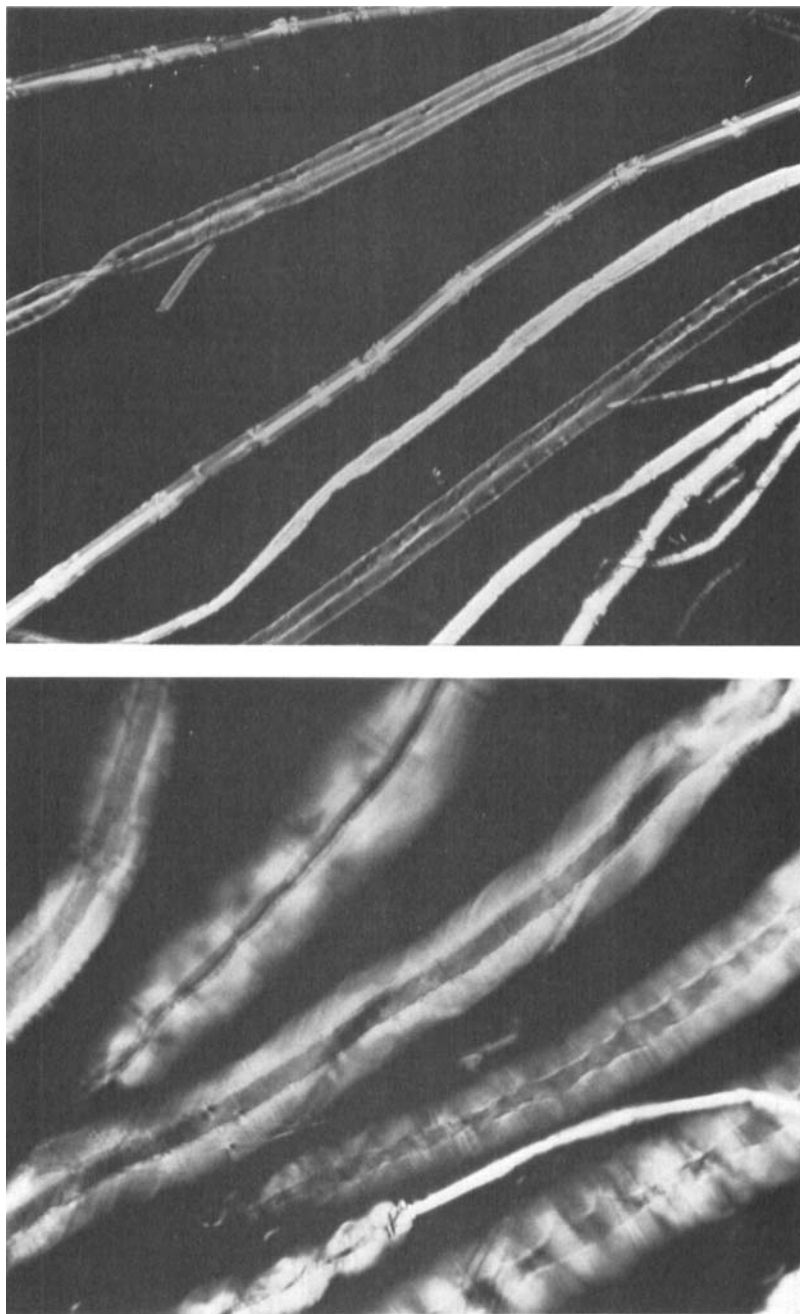


FIG. 1. Untreated (top) and treated (bottom) fibers as seen in the optical microscope.

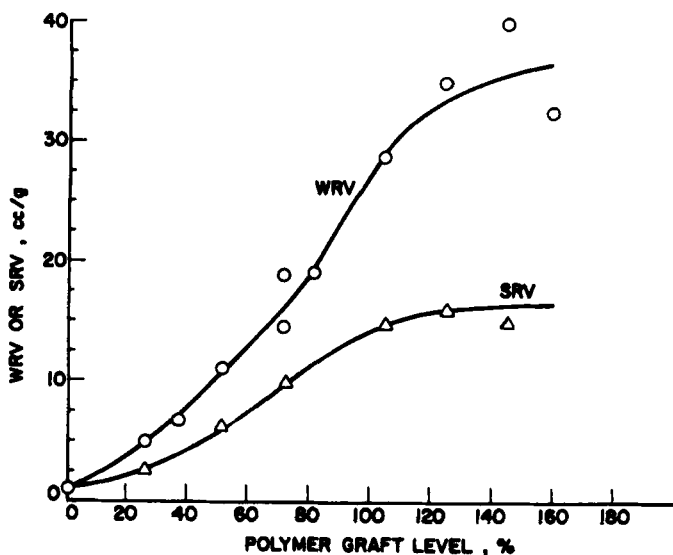


FIG. 2. Water (WRV) and 1% aqueous NaCl (SRV) retention value as a function of grafting level.

by fiber saturation point (FSP) measurements using the dextran solute exclusion technique of Stone and Scallan [7]. Thus the water is present in the fiber wall rather than in the lumen or the interfiber capillaries.

While ratios of 20 to 25:1 between the WRV of treated and untreated fibers are obtained at a water activity of unity, the situation is different as the water activity decreases. As seen in Fig. 3, the sorption of water in the grafted sample is only about 4 times that of the untreated fibers in the lower activity range.

Since the polymer is a polyelectrolyte and can be converted to its nonionized carboxylic acid form by adjustment of the pH, it could be expected that the water absorbency would vary with the pH. Figure 4 shows this effect. As the pH is reduced by adding HCl, the sodium carboxylates are converted to carboxylic acid groups, and at pH 3.75, where the acid form is not ionized, the fibers are deswollen, and their WRV is similar to that of the untreated pulp. When NaOH is added to the washed acidified fibers at pH 3.7, the reverse phenomenon is observed but with hysteresis. However, WRV is related to the extent of conversion to the sodium carboxylate form as shown by the numbers in parentheses.

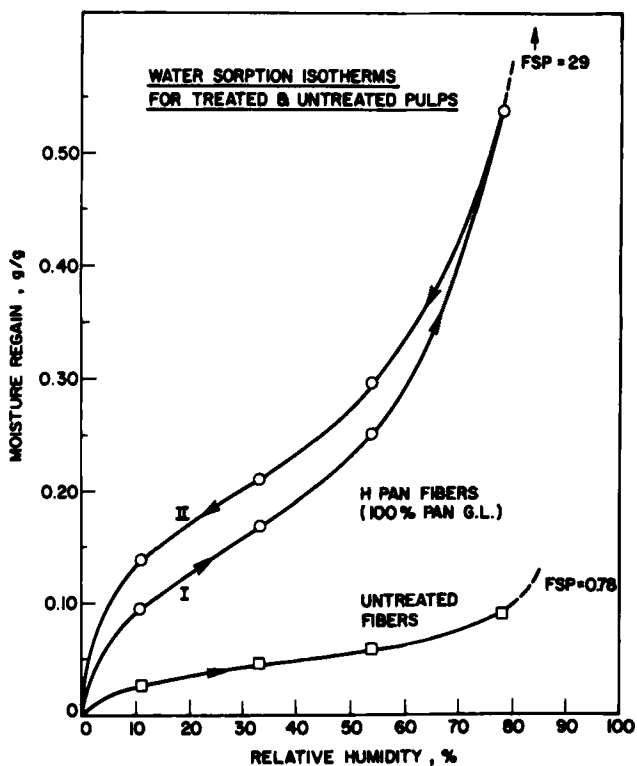


FIG. 3. Water sorption isotherm for grafted and ungrafted fibers. The fiber saturation points (FSP) are obtained by solute exclusion.

Swelling and Its Relationship to Grafting Level

At the PAN graft stage, the fibers are not swollen. After hydrolysis the polymer becomes water soluble and ionizes. Osmotic effects lead to the development of swelling pressure. In addition, since the polymer is a fully ionized polyelectrolyte, there may be additional swelling forces generated by the chain extension. These swelling forces will act until they are balanced by restrictive forces arising from the inherent structure of the cellulose fiber.

The change in WRV with graft level and its variation with pH could then be explained by the increasing number of carboxylate groups as the graft level increases and of their degree of ionization as the pH

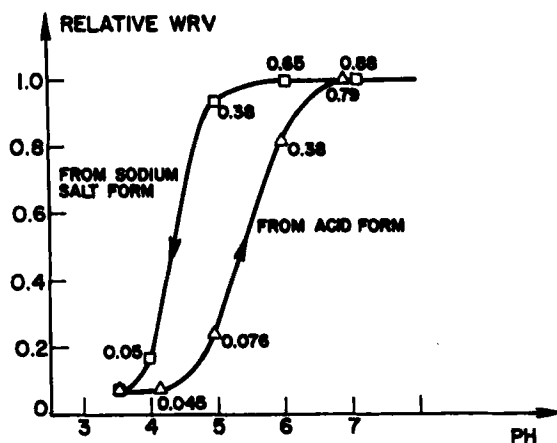


FIG. 4. Change in water retention value with pH. The values have been normalized. Values on curve indicate extent of conversion to sodium salt, expressed as $\frac{[\text{NaPA}]}{[\text{NaPA} + \text{HPA}]}$.

TABLE 1. Influence of Graft Level and Carboxyl Content on WRV

Polymer	Graft level (%)	Carboxyl content as poly(acrylic acid), (%)	WRV (g/g)
Poly(acrylic acid) ^a	21	17	3
Polyacrylonitrile	48	17	10
Poly(ethyl acrylate)	71	15 ^b	19.5
Polyacrylonitrile	21	9	3.5
Polyacrylonitrile	71	22	17.5

^aConverted to sodium salt.

^bExpected carboxyl content was 32%, but a considerable amount of polymer was lost during hydrolysis.

is changed. On the other hand, when the same number of carboxylic groups was introduced by other routes, no correlation was found between WRV and carboxyl content while a good correlation did exist between WRV and initial graft level, as seen in Table 1.

While the presence of the ionized polyelectrolyte is responsible for the development of swelling forces, it appears that the PAN

grafting stage per se was beneficial to the subsequent swelling phenomenon. It is believed that, during grafting, changes occur which lead to a weakening of the fiber structural cohesion. Expansion takes place already during grafting in the sense that the polymer does not merely fill in voids previously occupied by water but acts as a wedge and creates a new water-filled volume of approximately the same magnitude, as demonstrated in Table 2. The relative constancy of the water to cellulosic material volume ratio, as the amount of intruding polymer increases, would be expected if the polymerization were to take place inside the lumen or on the outside surfaces of the fiber leaving the bulk of the fiber intact. However, the optical micrograph of Fig. 1 and the fact that as little as 10% graft was sufficient to prevent dissolution of the fiber in cupriethylene diamine (a solvent for cellulose) leaves little doubt as to the uniformity and intimacy of penetration of the polymer within the fiber structure. As will be seen, this picture is reinforced by electron microscopic observation.

As to the polyacrylamide part of the copolymer, its role in determining the final swelling is primarily that of an interposed material which reduces the cohesion of the fiber elements.

Any treatment which would lead to a weakening of the fiber structure should then normally result in increased swelling. This was verified experimentally by beating the fibers, prior to grafting, as shown in Fig. 5, where the WRV and SRV of beaten and unbeaten grafted pulps are compared as a function of graft level.

TABLE 2. Volume of Water Associated with 1 g of Cellulose after PAN Grafting but Before Hydrolysis

Graft level (%)	Associated water (cm ³ /g)	
	From WRV ^a	From FSP ^b
0	1.30	1.30
40	1.22	1.31
65	1.13	-
125	1.15	1.38

^aCalculated from WRV measurements.

^bCalculated from fiber saturation point measurements.

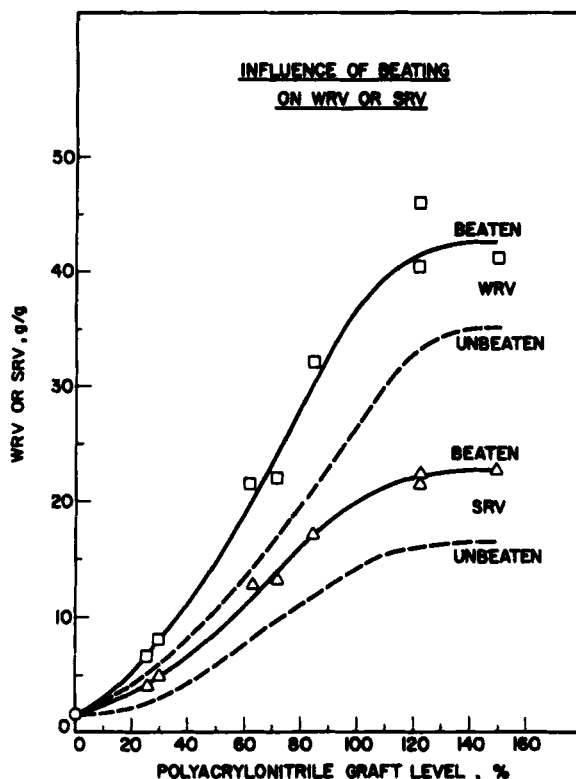


FIG. 5. Influence of beating on WRV and SRV of grafted fibers.

Colloidal Solutions

Rather than considering these fibers as containing 30 to 40 times their weight of water, one may look at them from a different view point, as an aqueous system containing 2.5 to 3% solids. Indeed, when a suspension of these fibers, which have retained their structural integrity during swelling, was subjected to a high shear field such as that which develops in a Waring Blendor, it was rapidly transformed into a gel-like, very viscous, colloidal solution exhibiting pseudoplastic, thixotropic behavior.

Figure 6 shows the effect of graft level on the solution turbidity. A minimum graft level is required before complete disaggregation of the fibers occurs. This minimum is around 40 to 50%. As the PAN graft

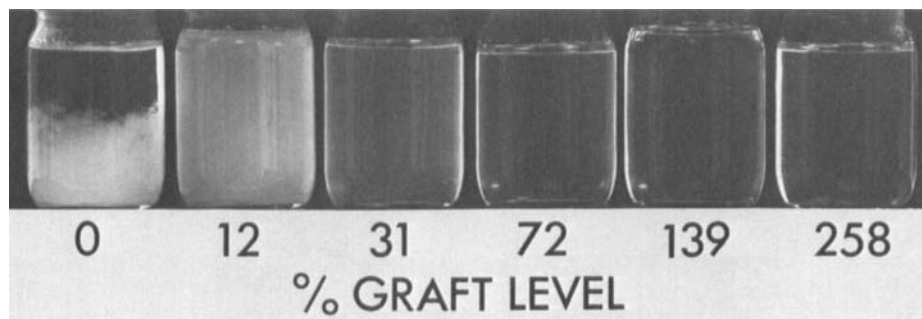


FIG. 6. Changes in solution turbidity versus PAN graft level.

level increases to 70 to 80%, the solution becomes much clearer and turbidity decreases only marginally thereafter.

Figure 7 shows typical viscosity curves as a function of polymer composition and concentration at 20 sec^{-1} shear rate. It is seen that a sharp maximum occurs at a polymer composition of 50 to 55% polyacrylamide-sodium polyacrylate copolymer, 45 to 50% cellulose, i.e., practically at the level where the solution turbidity disappears. Then the viscosity decreases to reach the low value for the homopolymer. When a film obtained by drying the colloidal solution was observed in the transmission electron microscope, a random dispersion of long, thin, rodlike particles was seen, Fig. 8. The lateral dimension of these particles is of the same order of magnitude as that of a protofibril, the primary constituent of a wood fiber.

Since the polymer is a graft copolymer, part of the anomalously high viscosity could be ascribed to the long "effective chain length" of the graft. However, it is believed that another effect may be predominant, and that is the presence of thin, long, rodlike particles requiring a very large volume to move about. As the grafted polymer content increases, there is a corresponding increase in molecular weight of the graft so that the effective chain length continues to increase. But the viscosity decreases. On the other hand, as the grafted polymer content increases, for the same overall concentration, the number of rodlike particles per unit volume decreases, so that if this effect is predominant, there should follow a corresponding decrease in viscosity. This is the case here.

In fact, if one tries to connect points of equal cellulose concentration (the tie-lines of Fig. 7), i.e., points of equal concentration of rodlike particles, we see that viscosity does not vary greatly.

It seems then that the grafted polymer acts in a synergistic way to further reduce the mobility of the cellulose rods. The behavior

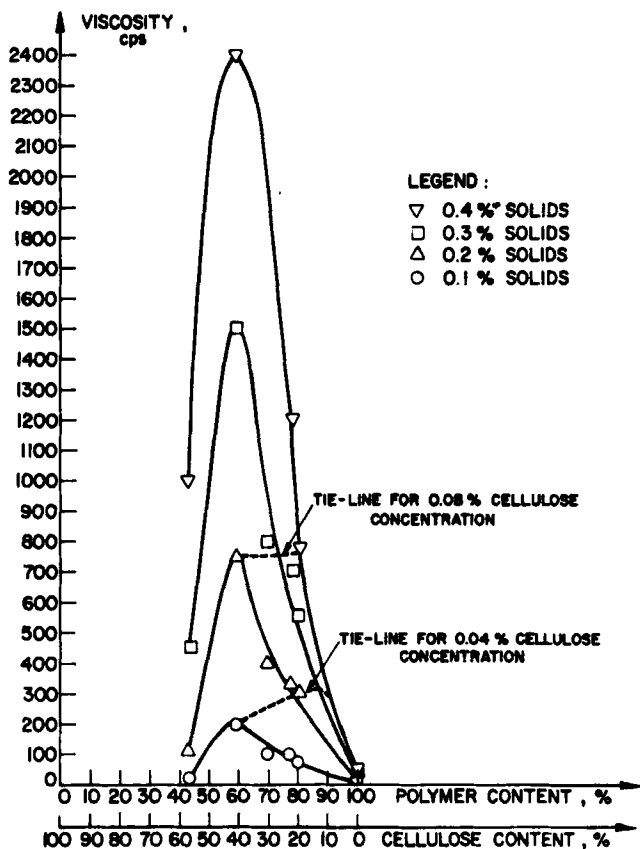


FIG. 7. Viscosity of colloidal solution at 20 sec^{-1} shear rate versus graft copolymer composition and concentration.

of the system is consistent with the idea that the viscosity is primarily due to the cellulose rods themselves and the role of the grafted polymer chains is to stabilize the dispersion by protective colloid action. The stability of the dispersion is, however, reduced or destroyed by the addition of acid or electrolyte and results in a drop in viscosity and the development of opacity. A polymer content of approximately 50% is sufficient to permit complete disaggregation of the fiber, leading to maximum viscosity development. Increasing the polymer content would not increase the degree of disaggregation but would have the net result of decreasing the effect of the rodlike particles on viscosity by decreasing their number at any given overall concentration.

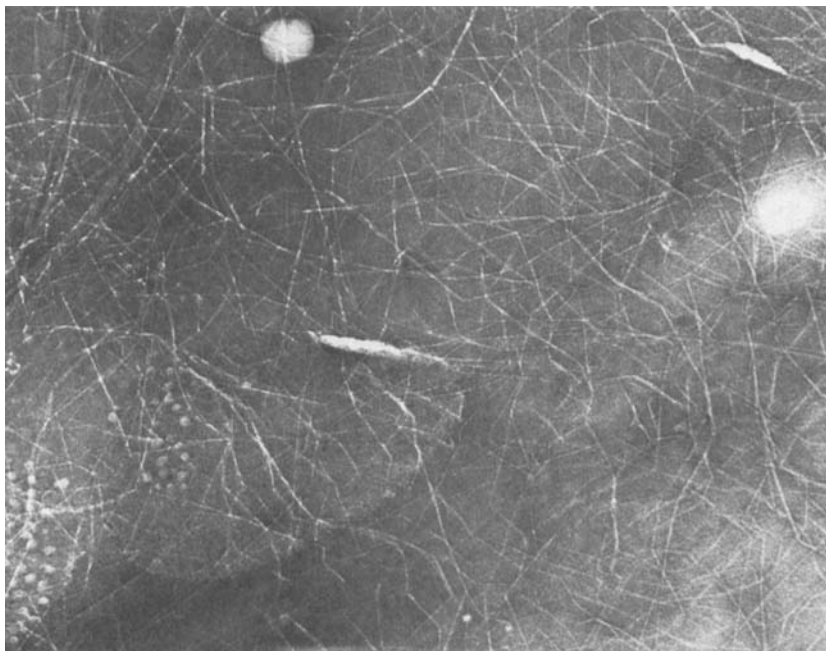


FIG. 8. Electron micrograph of film obtained by drying the colloidal solution. Original magnification $\sim 110,000\times$. Present magnification $\sim 825,000\times$.

CATIONIC POLYELECTROLYTE GRAFTS

The monomer used in this part of the study was dimethylaminoethyl methacrylate. Grafting was done by the xanthate- H_2O_2 process [8] with the monomer in the chloride salt form.

Water retention values were measured as a function of graft level. Even though the same trend was observed—WRV increased with graft level, the results were much less spectacular than those obtained with the anionic grafts, Fig. 9.

Since, as in the previous case, the polymer can exist in the non-ionized (amine) or ionized (salt) forms depending on pH, it is interesting to compare the changes in WRV with pH for the two types of polyelectrolytes, at the same graft level, i.e., at the same degree of polymer intrusion. The results are shown in Fig. 10. A reverse effect is observed because the cationic polyelectrolyte at pH 9 is in the non-ionized amine form and ionizes as the pH is reduced by addition of HCl.

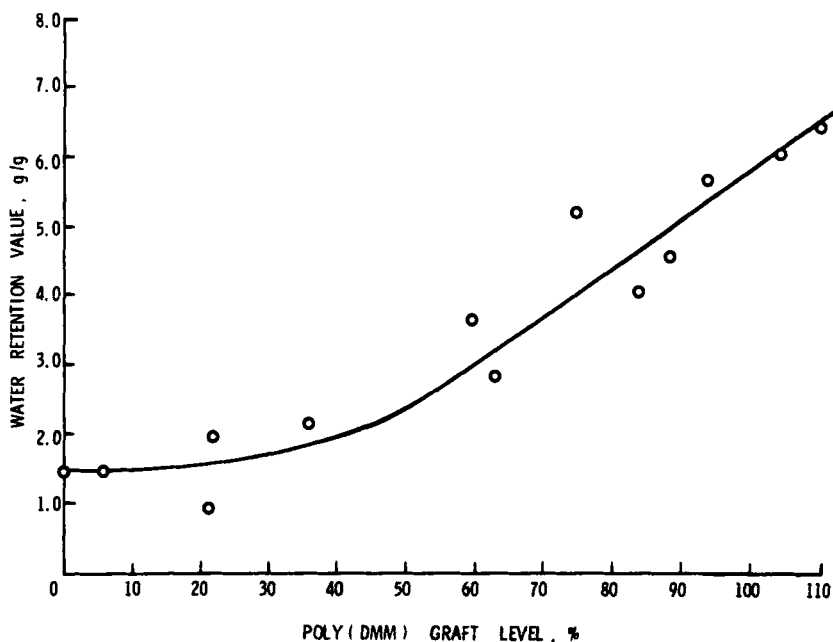


FIG. 9. Water retention value as a function of graft level for cationic grafted fibers ($\text{pH} = 4.5$).

The difference in the degree of swelling may be due to several factors. First, although the level of polymer intrusion is similar, there is a difference in charge density since the anionic polyelectrolyte carries 3.9 vs 2.6 meq/g for the cationic fibers (at 2.6 meq/g the WRV of the anionic graft is 16 g/g). Second, there may be a difference in the degree of hydration of the various groups. But one can also imagine that during grafting the bulky cationic monomer finds it more and more difficult to diffuse within the increasingly cationic environment so that the high level of grafting uniformity which was observed in the case of PAN, probably was not achieved here.

CONCLUSION

The novel properties that have been demonstrated are the result both of the presence of a large number of functional groups within the porous structure of the fiber and of their distribution along long flexible polymer chains. Graft polymerization provides an efficient and flexible method of introducing such groups to the extent desired while the overall fiber structure remains relatively intact.

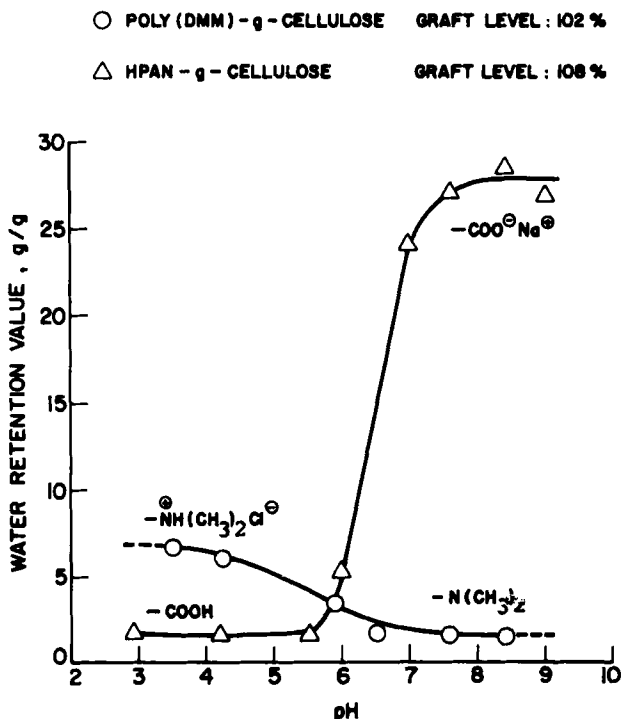


FIG. 10. Water retention value versus pH for cationic and anionic polyelectrolyte grafts.

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