

Swelling of Anionic and Cationic Starch-Based Superabsorbents in Water and Saline Solution

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Synopsis

Starch graft superabsorbents were prepared by graft copolymerization either with polyacrylonitrile (PAN) and saponification of the resulting copolymer or with trimethyl-aminoethylacrylate chloride (CMA) and methylene bisacrylamide as crosslinking agent. The influence of several structural parameters on the swelling properties of these absorbents have been studied: crosslink density, ionic content, and composition of the starch. As expected, the absorbency decreases with an increase of the crosslink density. It increases with the ionic content of the graft copolymer up to a maximum, an excess of charges leading to a swelling decrease. The PAN branch length depends on the origin of the starch. High molar weight PAN was grafted onto waxy corn, a starch with high amylopectin content. The swelling increases with increasing molar weight of PAN up to 5×10^5 . In saline solution the absorbency of both ionic gels decreases significantly. However, in the presence of multivalent ions their behavior is different. For cationic absorbents the swelling depends on the ionic strength but not on the ion valency. On the other hand, anionic absorbents are significantly affected by multivalent cations.

INTRODUCTION

Renewed interest in highly water absorbing materials obtained by graft copolymerization on polysaccharide has developed.¹⁻⁹ In a previous paper¹⁰ polyacrylonitrile (PAN) was grafted to various starches and we have studied the influence of the starch composition on the structure of the grafted polysaccharide (graft length, frequency). Grafting onto waxy corn promotes PAN branches of high molar weight and the resulting hydrolyzed copolymers have a high absorbency in water.

In this paper we report the influence of several structural parameters on the swelling properties in water or saline water of starch-based superabsorbent gels. The ionization of the polymer network has an important role on the swelling behavior. In saline water, the charges on the polyion are screened by counterions and significant deswelling is observed.

Both anionic and cationic superabsorbent gels have been prepared. Anionic gels were obtained by saponification of graft PAN onto starch. Crosslinks and sodium acrylate units are formed during the alkaline hydrolysis. Cationic gels have been synthesized by graft copolymerization with a cationic monomer (trimethylaminoethylacrylate chloride) (CMA) and a crosslinking reagent [*N,N'*-methylenebis(acrylamide)]. The relation between the structure of both

gels and their swelling behavior in water or in saline water is studied.

EXPERIMENTAL

Syntheses

The polyacrylonitrile graft polymerization on various starches and the saponification reaction have already been described and the graft characteristics given elsewhere.¹⁰ The amperometric titration method used to determine the percentage of amylose in the starch has also been reported. The percentage of grafted polyacrylonitrile was obtained from the weight of starch after soxhlet extraction with DMF. After the complete degradation of starch by acid hydrolysis, the molecular weight of polyacrylonitrile recovered was determined from viscosity measurements.

The cationic monomer, CMA (Hoechst), was recrystallized from isopropanol before use. In a 250 mL reactor, 2 g of starch (Roquette, Avebe or Merck) and 35 cm³ H₂O were introduced. The slurry was heated to 85°C for 1 h under nitrogen atmosphere. The heating was stopped and the freshly prepared initiator [36 mg of Ce(NH₄)₂(NO₃)₆ in 0.6 cm³ 1N HNO₃] was added when the temperature reached 30°C. Five minutes later, the monomer mixture [9.77 g of CMA, 3.55 g acrylamide (AM), and 15 mg of methylene bisacrylamide] was added and the slurry kept at 30°C for 2 h. Then 100 mL H₂O were added and the gel was separated by filtration under vacuum, washed with methanol, precipitated in acetone, and dried under vacuum at 40°C.

These cationic graft copolymers are highly hygroscopic and contain 10% by weight of water. Their cationic content was determined by microanalysis and potentiometry, the chloride counterion titrated with AgNO₃ using a Tacussel unitubular Ag-Hg/Hg₂SO₄ electrode. The cationic charge content is given by % CMA = number of moles of CMA/AM + CMA.

Grafting CMA, acrylamide, and a crosslinking agent onto starch with the redox system sugar/Ce⁴⁺ gives yields higher than 90%. Crosslinking leads to high conversion of the monomers and to a percentage of graft polymer higher than 75%. Without the crosslinking agent the percentage of acrylamide and CMA grafted onto starch decreases drastically and no gel is obtained. For a feed composition of the cationic monomer higher than 50%, the CMA content of the resulting copolymer is less than 45%.

An anionic gel was also prepared by copolymerization of sodium acrylate with acrylamide according to the following procedure: 0.166 mol acrylamide, 29.2 mmol acrylic acid (85% acrylic groups were neutralized by NaOH) and 1.1 mmol methylenebis acrylamide were introduced in 70 mL deionized water. Air was flushed from the reaction vessel by nitrogen for 30 min. Then 0.1 g of (NH₄)₂S₂O₈ dissolved in 5 mL H₂O and 0.083 g of NaHSO₃ dissolved in 5 mL H₂O were introduced in the reactor with vigorous stirring. The solution was kept at room temperature for 3 h. After gelation the material was swollen in an excess of water during 15 h to remove the uncrosslinked chains, then deswollen in acetone, and dried at 50°C under vacuum. The gel is characterized by potentiometric titration and microanalysis. It contains 35% of acrylate groups and 0.5% of crosslinks.

Liquid Retention

The gels were soaked either in deionized water (Milli-Q Millipore system) or in synthetic urine until equilibrium was reached and their absorption capacity was determined by weighing the swollen gels on a sieve to constant weight.

The procedure was as followed. Granules of 100–200 μm were swollen in water and washed until the pH of the liquid phase was about 9. After swelling equilibrium had been reached (3 days), 100 g of gel were weighed on a sieve (mesh: 100 μm), then precipitated in acetone, and dried at 40°C under vacuum. The absorbency q is expressed in grams of water retained in the gel by a gram of dried gel (g/g).

The retention capacity of the gels in synthetic urine (composition: 0.64 g CaCl_2 ; 1.14 g MgSO_4 ; 7 L solution H_2O ; 8.2 g NaCl ; 20 g urea and water) has been also determined.

Percentage of Solubles

m grams of gel were soaked in water. After the equilibrium had been reached the gel was dried and weighed again (m'). The percentage of solubles was calculated from the relation:

$$\frac{m - m'}{m} \times 100 \quad (1)$$

Kinetics of Swelling

After addition of the superabsorbent to pure water, the viscosity of the dispersion changes with time and a critical gelation time, characteristic of the structure of the gel, can be determined when the viscosity diverges. But difficulties due to the granular nature of the dispersion and to the shear of the gel are encountered with this method. Therefore, a technique based on capillary suction was preferred (Fig. 1). A graduated burette with an air inlet at the bottom was linked by a flexible tube to a cell covered with a metallic grid. After filling with water, the burette was closed at the top and air was introduced. One hundred milligrams of gel were placed on the grid. The water adsorbed by the sample and the swelling kinetics were easily followed. Data fit the following empirical relation:

$$Q = Q_e(1 - e^{-\alpha t}) \quad (2)$$

where Q_e is the swelling maximum, $\alpha = 1/\tau$, and τ is the swelling characteristic time.

The swelling kinetics for a starch-*g*-polycationic copolymer (cationic unit content: 30%) is given in Figure 2 as an example.

RESULTS AND DISCUSSION

The swelling of absorbents depends on both the structure of the network and the nature of the liquid. The structure of the gels can be controlled by several parameters adjustable during the synthesis: nature of the charge, ionic

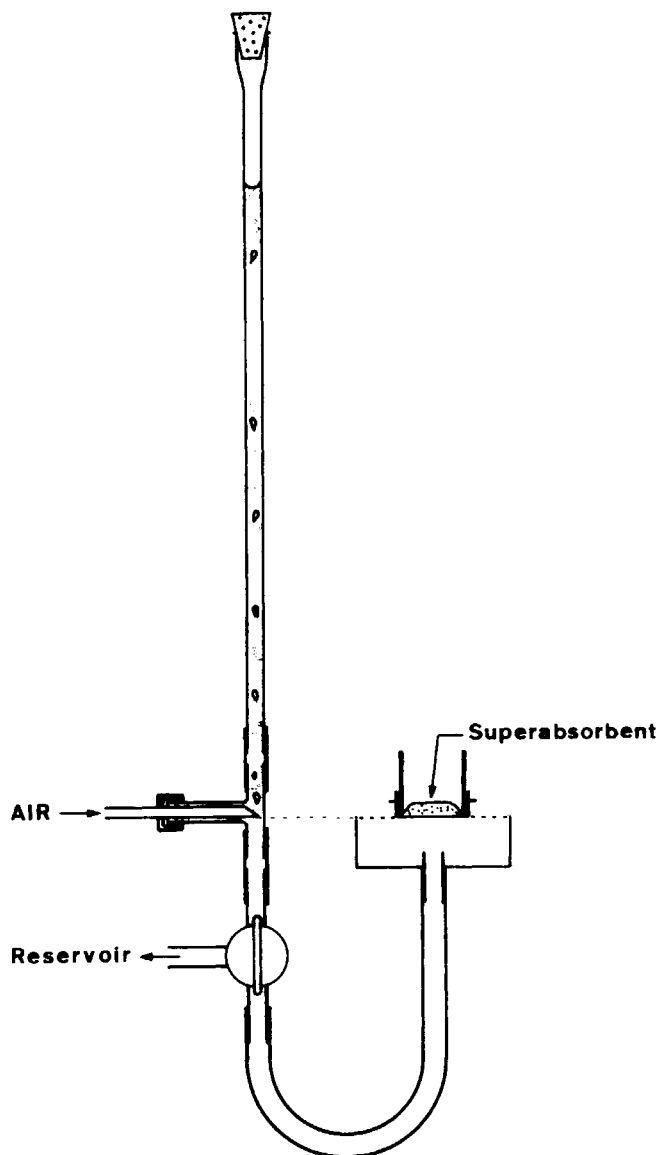


Fig. 1. Capillary suction apparatus.

unit content, crosslinking density, and graft length. The relation between these molecular parameters and the swelling behavior is studied.

Ionic Unit Content

It is well known that the extensive swelling of hydrogels is induced by the electrostatic repulsion of the ionic charges of the network. The ionic charge content is difficult to control during the saponification of the starch graft polyacrylonitrile and this parameter was investigated with a series of cationic gels. Figure 3 shows the liquid retention (water or synthetic urine) as a

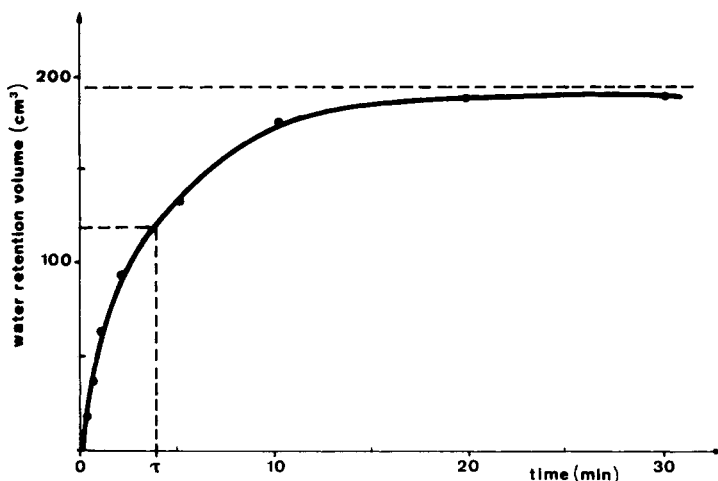


Fig. 2. Swelling rate for a starch graft cationic absorbent (CMA 30%) $Q_e = 190 \text{ cm}^3 \text{ g}^{-1}$; $\tau = 230 \text{ s}$.

function of ionic charge content of the copolymer. The gel with about 35% CMA shows the highest absorbency. Thereafter the absorbency decreases with ionic content. This behavior may be the result of a delicate balance between long range electrostatic forces, condensation of counterions on the polyion, and ionic strength.

Buchanan et al.¹¹ have plotted the water retention of polyacrylate networks as a function of the degree of neutralization and they also observed a swelling maximum. They suggested that the chain could expand to such an extent that the distance between neighboring charges becomes too great for optimum cooperation effects between the charges.

The rheology of cationic gels has been studied by Opperman.¹ He observed an increase of the elastic modulus and of the number of effective chains in the network with the cationic content.

Several viscometric studies on linear polyelectrolytes with variable charge density have been reported. For a series of hydrolyzed polyacrylamides, Muller et al.¹² observed that the intrinsic viscosity goes to a maximum when increasing the ionic content. Likewise the intrinsic viscosity of linear acrylamide and CMA copolymers increases with the CMA content, but reaches a limit for a cationic unit content higher than 30%.¹³ This behavior was ascribed to an increase in chain stiffness and to counterion condensation on the polyion.

According to Manning,¹⁴ there is condensation of counterions on a polyion when the charge density λ is higher than a critical value given by

$$\lambda_c = \frac{4\pi\epsilon k_B}{e} T |z_i| = 2.26 \cdot 10^{-10} \text{ cm}^{-1} \quad (3)$$

in water at 20°C, where ϵ is the dielectric constant, k_B the Boltzmann constant, e the charge of the electron, and z_i the valence of the ion. For the ionic gels studied here, the charge density of the polyion between two

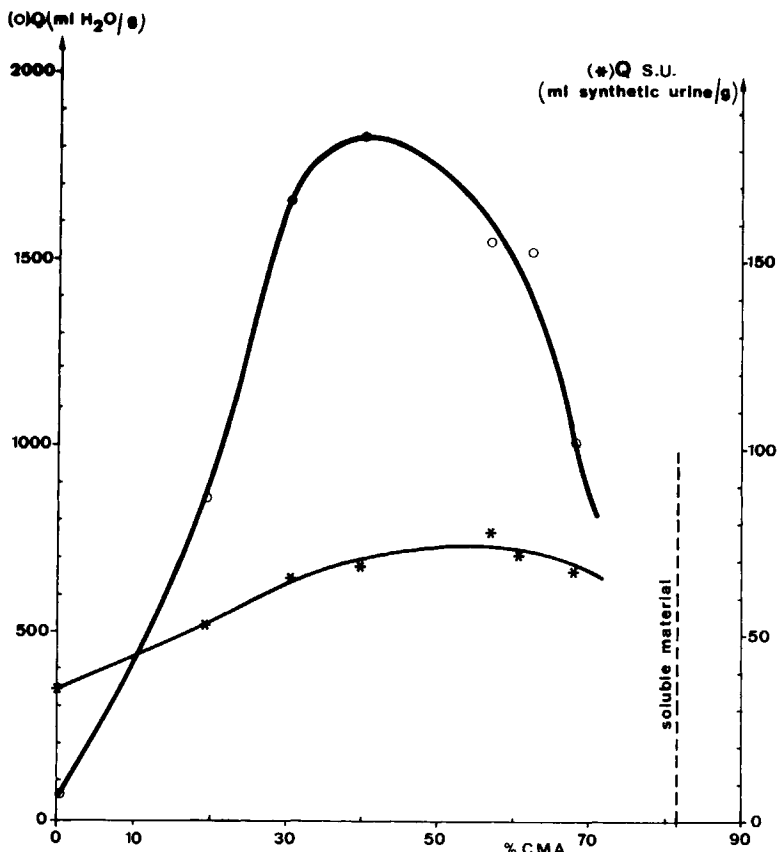


Fig. 3. Absorbency of cationic absorbents as a function of CMA content in deionized water and synthetic urine.

crosslink points was calculated from the relation

$$\lambda = |z_i|eN_c\alpha/L \quad (4)$$

where N_c is the mean number of segments between successive functions, α the cationic unit mole fraction, and L the length of the extended chain. The equality $\lambda = \lambda_c$ is obtained when $\alpha = 0.35$. Figure 3 shows that the swelling increases up to about 35% of CMA. Thereafter it decreases in agreement with the α value calculated from Eq. (4) and assuming $\lambda = \lambda_c$. Counterions condense on the chain decreasing the charge density.

In solution of high ionic strength like simulated urine (a mixture of univalent and bivalent salts), the retention capacity of cationic superabsorbents is about 20 times lower in comparison with the gel swelling in deionized water. A maximum at about 35% CMA is also observed.

When the percentage of CMA in the monomer mixture exceeds 70% no gel is formed. For this composition the poor incorporation of the crosslinking agent in the graft copolymer is probably due to its low reactivity ratio.

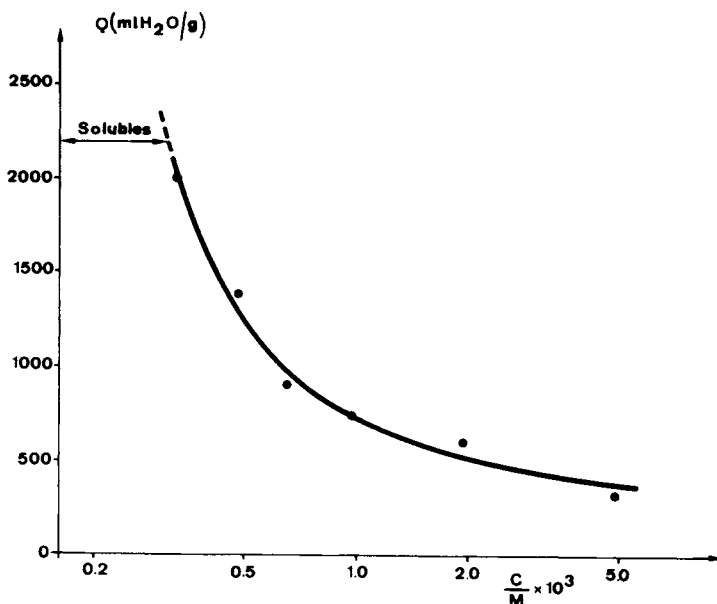


Fig. 4. Absorbency of cationic absorbents as a function of the crosslink density (C/M).

Crosslink Density

This parameter was studied with a series of cationic absorbents because the crosslinking agent was added to the monomer mixture for their syntheses. Figure 4 shows that the swelling decreases drastically with the crosslink density. A very low percentage of crosslinking agent yields gels with high retention capacity. The chains between junction points are then very extended.

Influence of the Initial Monomer Concentration

The polymerization rate depends on the monomer concentration. So the gelation time increases with dilution.

Figure 5 shows the absorbency as a function of the reaction volume for the synthesis of cationic absorbents. The higher the dilution of the reaction mixture, the higher the water retention of the gel. However, the material gets a poor consistency. The percentage of linear copolymers increases with dilution and high dilution can even prevent the gel formation. On the other hand, concentrated reaction mixture leads to gels with low swelling.

Saponification of Starch Graft Polyacrylonitrile

Influence of the Base/Acrylonitrile Ratio

During the alkaline hydrolysis of polyacrylonitrile at 80–100°C converting the nitrile group into a mixture of amide and carboxylate groups, intermediate colored products are formed.^{15–18} The coloration was attributed by Grassie to

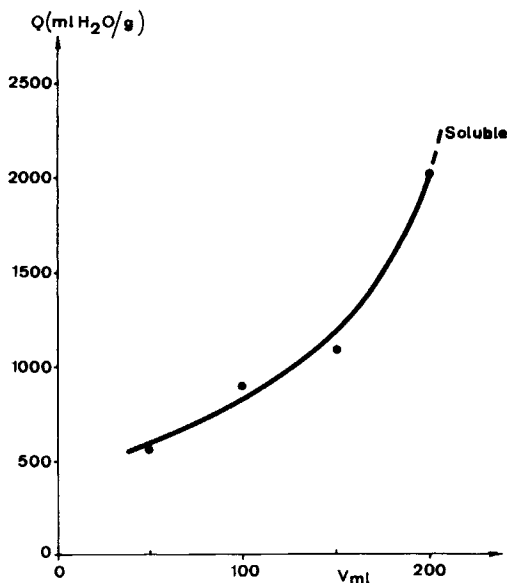
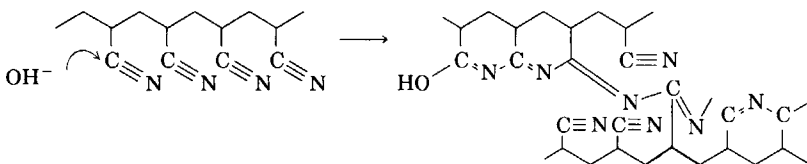


Fig. 5. Absorbency of cationic absorbents as a function of the reaction volume for the CMA graft copolymerization. Experimental conditions: 6.2 mmol AGU; 72 mmol AM; 30 mmol CMA; 64 μ mol crosslinking agent; 33 μ mol initiator.

the formation of a partly hydrogenated naphthiridine type structure which is initiated by the nucleophilic attack of OH^- on the carbon atom of the nitrile group. Insolubility of the polymer is known to occur during this step and is explained by "propagation crosslinks" between interchain neighboring nitrile groups:



The end of the reaction is characterized by the light yellow color of the solution indicating the disappearance of the conjugated system ($>\text{C}=\text{N}-$)_n and the formation of CONH_2 and CO_2^- groups. Evidence of crosslinks occurring during the alkaline hydrolysis was obtained: after acid hydrolysis of starch grafted PAN for starch removal, PAN chains were hydrolyzed in alkaline conditions leading to an ionic gel.

The percentage of acrylate groups formed by hydrolyzing the polyacrylonitrile graft depends on the base concentration. The influence of the OH^-/AN ratio on the gel absorbency has already been reported in a previous paper.¹⁰ The swelling increase is due to an increase of the ionized groups and to the cleavage of some interchain crosslinks. However, a maximum is observed. Thereafter, high OH^-/AN ratios lead probably to the cleavage of numerous ketimine crosslink points increasing the percentage of soluble chains. So chain

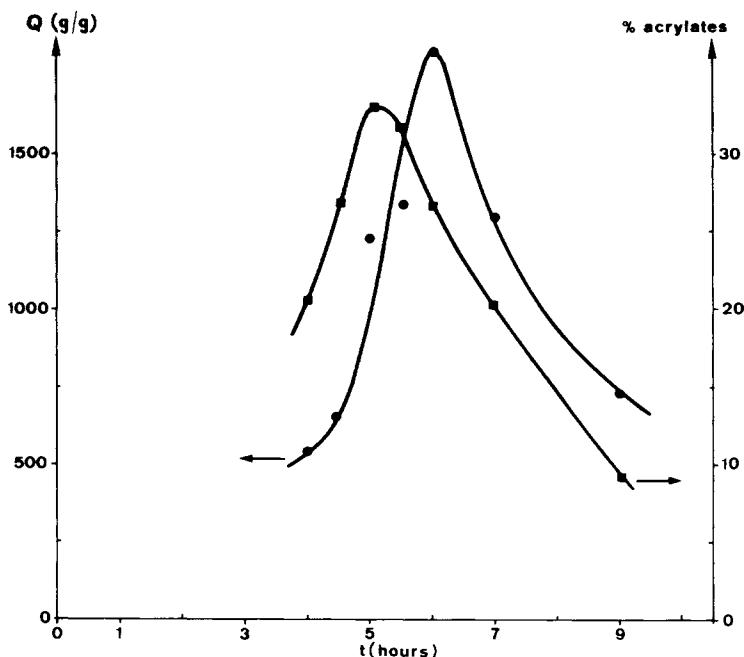


Fig. 6. Absorbency and percentage of acrylate groups as a function of the hydrolysis time.

degradations can explain the decrease of absorbency of gels obtained by saponification with concentrated base.

Temperature

When the reaction is carried out at room temperature, the slurry is still orange after 6 days, indicating the presence of conjugated double bonds $—C=N—C=N—$ in the material. Likewise, at 50°C , only partial hydrolysis is obtained. The slurry is decolorized when heating to 80°C . By increasing the base concentration the decoloration time decreases, but a water-soluble material is formed.

Hydrolysis Time

The percentage of CO_2^- in the hydrolyzed copolymer depends also on the time of saponification. Figure 6 shows the water absorbency and the number of acrylate groups as a function of time. The percentage of ionized groups and the swelling increase with time up to a maximum. Thereafter chain scissions occur leading to a loss of the polymer grafted onto starch. The maxima of both curves do not concur. The shift can be attributed to decarboxylation reactions and to the solubilization of short chains.

The time of hydrolysis and the OH^-/AN ratio are related parameters. Figure 7 shows that the maximum of swelling is shifted to longer time of reaction when the OH^-/AN ratio decreases.

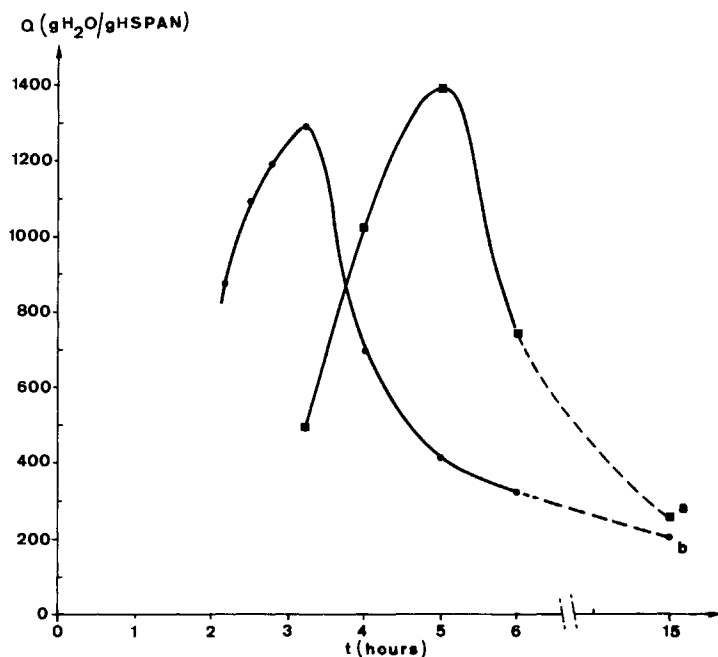


Fig. 7. Retention capacity as a function of the time of hydrolysis and OH^-/AN ratio. Experimental conditions: 500 mg starch grafted PAN; 20 mL NaOH; $T = 90\text{--}95^\circ\text{C}$. (a) $\text{OH}^-/\text{AN} = 1.1$; (b) $\text{OH}^-/\text{AN} = 1.3$.

TABLE I
Influence of the Base

Base	Q (g/g)	Q_{US} (g/g)	% Soluble polymer
KOH	550	40	30
NaOH	650	60	35
LiOH	1060	100	30

TABLE II
Characteristics of Hydrolyzed Starch Polyacrylonitrile Absorbents^a

Starch origin	% Amylose	% Grafted PAN	\bar{M}_n PAN	Discoloration time	% Acrylate	Q (g H ₂ O/g dry)
Waxy corn	0.5	55.0	870	1 h 30 min	36.0	1160
Manioc	18.0	53.5	860	1 h 50 min	31.0	1550
Potato	20.0	57.5	920	2 h 30 min	40.0	1280
Corn	25.0	48.0	840	1 h 30 min	29.0	1320
Wheat	27.0	53.0	670	1 h 30 min	22.5	930
Amylomaize	65.0	50.0	410	1 h 50 min	32.0	410
Amylose						
AVEBE	100.0	41.0	310	2 h 45 min	33.5	310
Merck	25.0	57.5	520	2 h 30 min	35.0	700

^a Experimental conditions: 300 mg of starch graft PAN hydrolyzed by 12 cm³ of 0.35N NaOH at 90–95°C during 2 h 45 min.

Nature of Base

Twenty cubic centimeters of 0.5*N* base solution are added to 500 mg of graft sample. The mixture was heated to 90–95°C during 2 h 30 min. The characteristics of the gels obtained are reported in Table I. Hydrolysis of starch grafted PAN with LiOH leads to gels with higher water absorbency.

Nature of Starch

We have already pointed out that the nature of starch and consequently the molar weight of the grafted PAN has a significant influence on the absorbency of the gel.¹⁰ So a gel prepared from waxy corn has a greater absorbency than a gel prepared from amylose AVEBE (Table II). The results are in agreement with those reported by Yamaguchi et al.⁹

To elucidate the influence of the molar weight of the graft on the absorbency of the gel, PAN grafts, obtained from acid hydrolysis of various grafted starches, were saponified. Despite the absence of starch, PAN chains were converted to ionic gels. This is in agreement with the hypothesis of chemical crosslink formation during the alkaline hydrolysis of PAN at

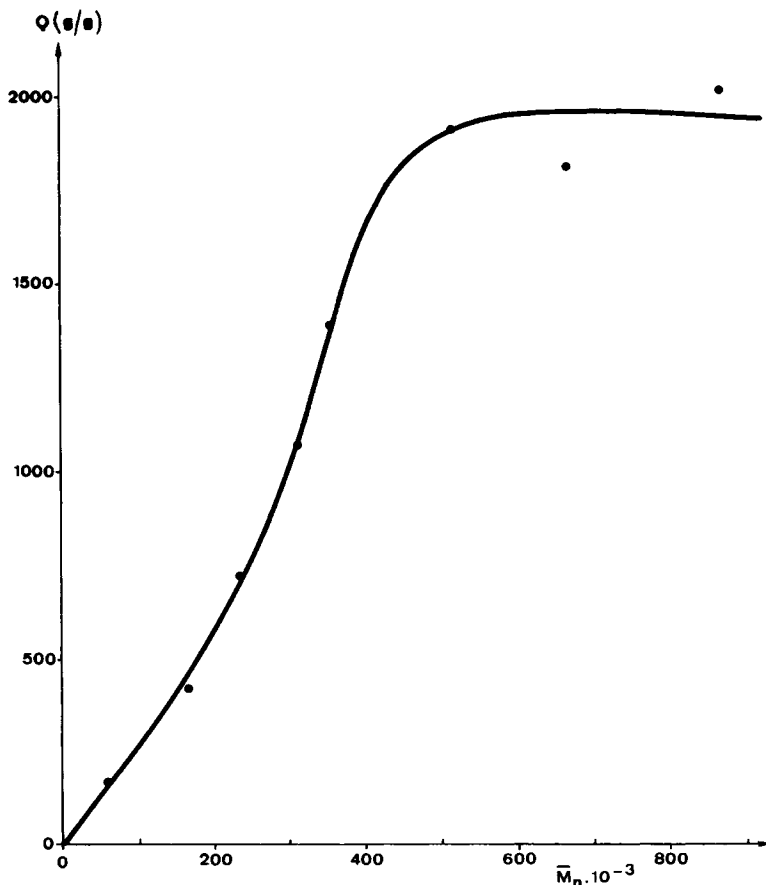


Fig. 8. Absorbency as a function of the molar weight of the anionic graft.

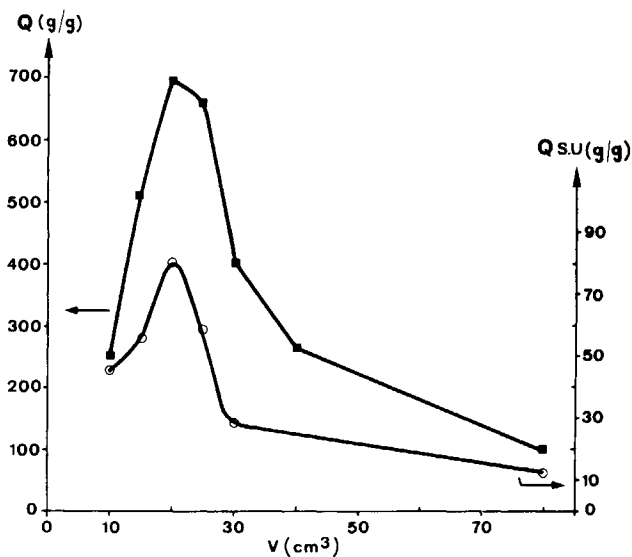


Fig. 9. Absorbency of an anionic gel: plots in synthetic urine (○) and in deionized water (■) against the volume of the saponification reaction.

90–95°C. By comparison with the starch based gels obtained in similar conditions, the absorbencies are two to three times higher. This effect can be attributed to a decrease of the effective weight of polyacrylate in starch-based absorbents, to different crosslink degrees, and to an increase of the gel stiffness by interpenetration of amylose and amylopectin chains in the polyacrylate network.

Figure 8 plots water absorbency against the molar weight \bar{M}_n of the graft (determined from viscometry).¹⁰ The swelling increases significantly with \bar{M}_n but tends to a limit at $\bar{M}_n \approx 5 \times 10^5$.

Reaction Volume

The swelling of the absorbent is plotted against the reaction volume used during the hydrolysis step (Fig. 9). It increases with dilution up to a maximum. Thereafter the rate of saponification is probably lower. As a result the swelling decreases.

Ionic Strength

Change in this external parameter will also affect significantly the swelling of the absorbent. Figure 10 shows the swelling of an anionic gel as a function of the saline concentration. The decrease of the expansion of the network is due to screening of the ionic charges bound to the network and to the decrease of the osmotic pressure difference between the gel and the external solution when the ionic strength increases. The effect of the ionic strength on the swelling has been determined using the relation suggested by Hermans¹⁹:

$$Q_e^{5/3} = A + Bv^2/I \quad (5)$$

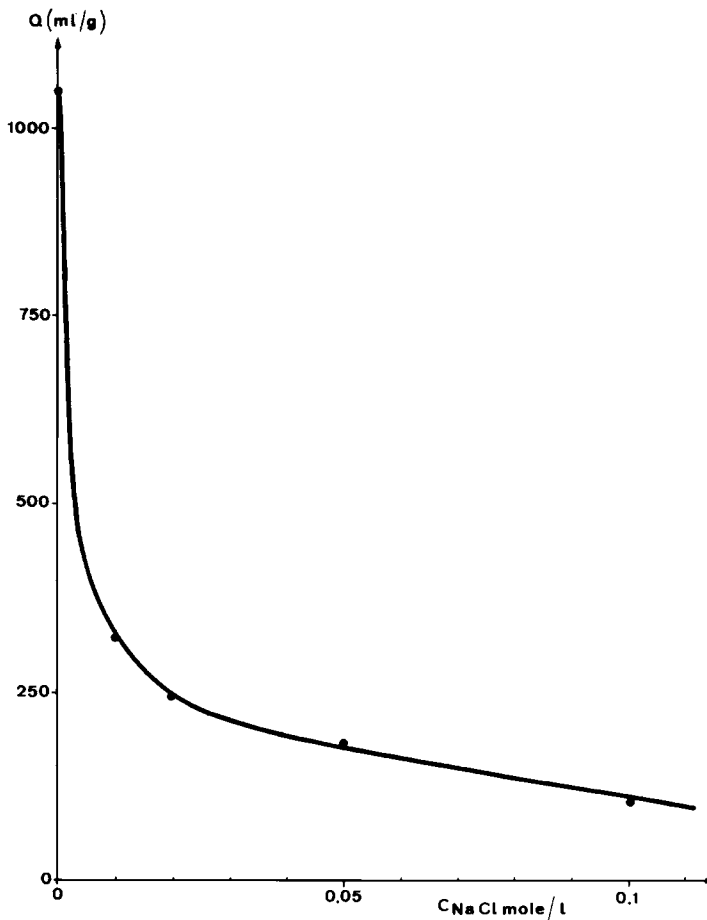


Fig. 10. Influence of NaCl concentration on the absorbency of a hydrolyzed PAN starch graft copolymer.

where Q_e is the retention at equilibrium, i the concentration of the charges bound to the gel, I the ionic strength of the external solution, and A and B are empirical parameters.

Good linear relationships are obtained for high ionic strength. But a discrepancy is observed for low I values, the swelling forces being counteracted by the elastic forces of the crosslinked chains (Fig. 11).

The ionic strength of the solution depends on both the mobile ion concentration and their valency. Small quantities of divalent or trivalent ions can decrease drastically the swelling values. This effect is shown in Figure 12 for a hydrolyzed starch graft polyacrylonitrile (CO_2^- 35%). This decrease, more significant with Ca^{2+} ions, can be due to the complexing ability of carboxylate groups inducing intramolecular and intermolecular complexes formation. Consequently, the crosslink density of the network increases.

The nature and the ion valencies of the saline solution have not so great an influence on the behavior of starch graft polyCMA gels (Fig. 13). The retention values determined respectively in NaCl and Na_2SO_4 or $MgCl_2$ and

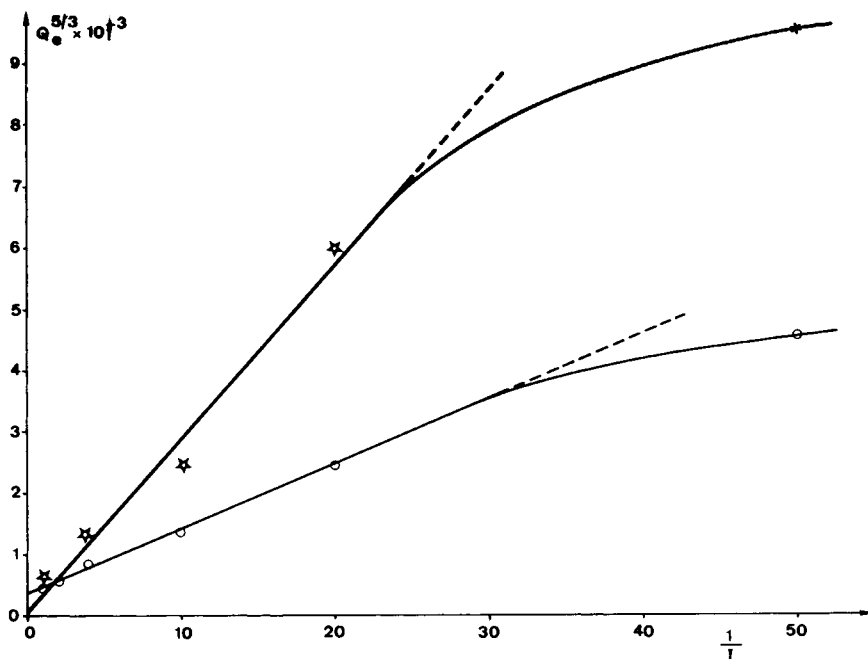


Fig. 11. Absorbency plots against the ionic strength I : (☆) hydrolyzed starch graft polyacrylonitrile (CO_2^- content 35%); (○) starch graft copolyacrylamide-CMA (CMA content 36%).

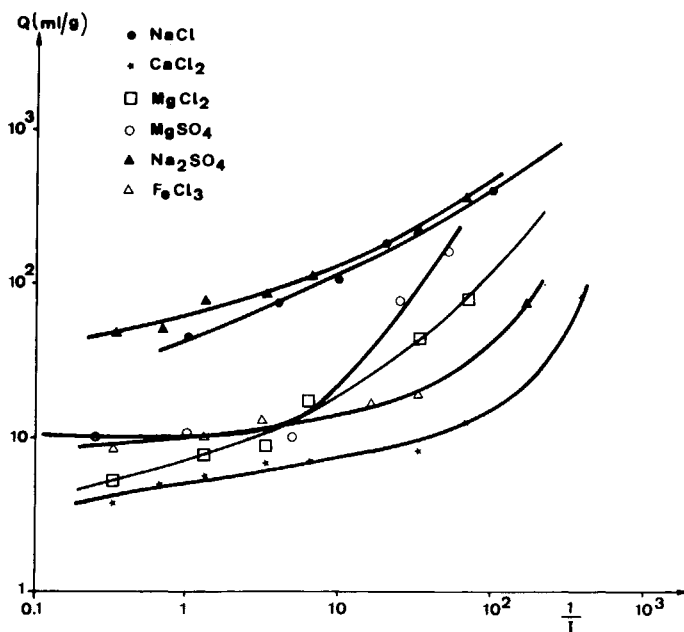


Fig. 12. Absorbency of a hydrolyzed starch graft polyacrylonitrile vs. I (CO_2^- content 35%): (●) NaCl; (★) CaCl_2 ; (□) MgCl_2 ; (○) MgSO_4 ; (▲) Na_2SO_4 ; (△) FeCl_3 .

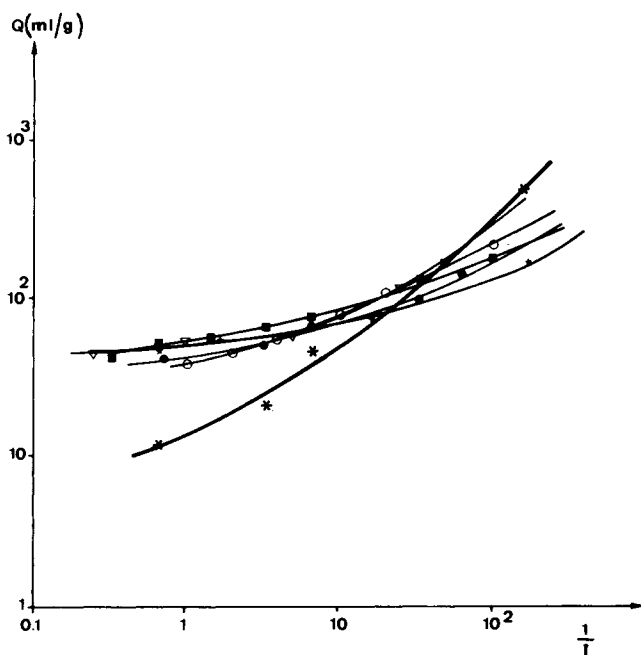


Fig. 13. Absorbency of a starch graft polyacrylamide-CMA vs. I (CMA content 36 %): (○) NaCl; (*) CaCl_2 ; (■) MgCl_2 ; (▽) MgSO_4 ; (●) Na_2SO_4 ; (★) FeCl_3 .

MgSO_4 solutions are similar. In CaCl_2 solution, the lower swelling values are interpreted as an increase of the crosslink density of the gel due to the complexation of Ca^{2+} with the acrylamide group.

This behavior is in agreement with the results reported by Gugliemelli et al.²⁰ on the viscosity of hydrolyzed starch polyacrylonitrile dispersions in various saline solutions. They showed that the viscosity of the dispersion decreased with an increase of the counterion valency.

Gel Transition

Small changes in an external parameter such as pH, temperature, or composition of solvent may induce a phase transition.²¹⁻²⁷ Figure 14 shows the retention as a function of NaCl composition for a poly(acrylamide-co acrylate) gel containing 32% of ionized groups. A discrete transition is observed between 5×10^{-3} and $10^{-3}M$ NaCl. The transition reduces the retention capacity from 330 to approximately 180 g water/g dry sample. A different behavior is obtained for starch grafted AM-CMA copolymers where two discrete volume changes are observed (Fig. 15) in the 10^{-4} - $10^{-5}M$ and 10^{-3} - $10^{-2}M$ NaCl concentration domains. Rodehed et al.⁸ reported the same swelling behavior for hydrolyzed starch graft PAN as a function of solvent composition of water/ethanol mixtures. They attributed the first transition to polymer/polymer affinity inducing the expulsion of free water from the network. The second transition is due to interactions between the polar molecules of the solvent and the ionic groups of the gel. The magnitude of this

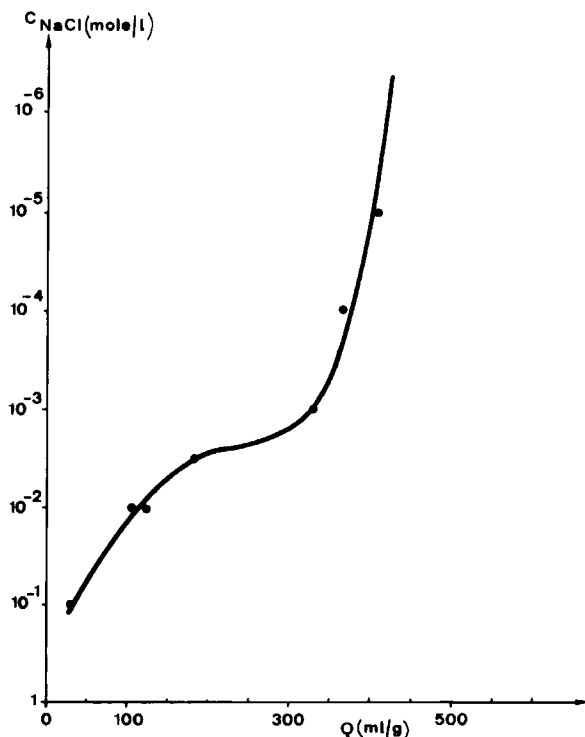


Fig. 14. Absorbency of a crosslinked poly(acrylamide-co-sodium acrylate) as a function of NaCl concentration.

transition increases when the starch backbone is cleaved by acid hydrolysis. So the presence of starch in the gel decreases its swelling degree and leads to a continuous swelling change with saline concentration.

Swelling Kinetics

Superabsorbents are also characterized by their high swelling kinetics. For example, 1 g of dry starch graft polyCMA can absorb up to 200 cm³ H₂O in 3 min.

The retention capacity is a combination of effects due to the degree of crosslinking and to the ionization degree in the gel.

Kinetics of swelling of spherical polyacrylamide gels described by the model of Tanaka and Fillmore²⁸ has been generalized by Candau et al.²⁹⁻³² They consider a single isolated gel sphere partly swollen and put in an excess of solvent. There is an osmotic pressure shock and the gel swells to reach a new equilibrium volume. The evolution of the sphere radius to its equilibrium value is described by an infinite sum of exponential decay, but the final steps of the swelling process can be described by a single exponential relaxation. The influence of the crosslink density of the network on the kinetics of swelling has been investigated for a series of starch graft polyCMA with a method described in the Experimental section. The volume of water absorbed by a piece of dry gel is determined as a function of time. The swelling changes exponentially. From eq. (2) a characteristic time is defined for which $Q =$

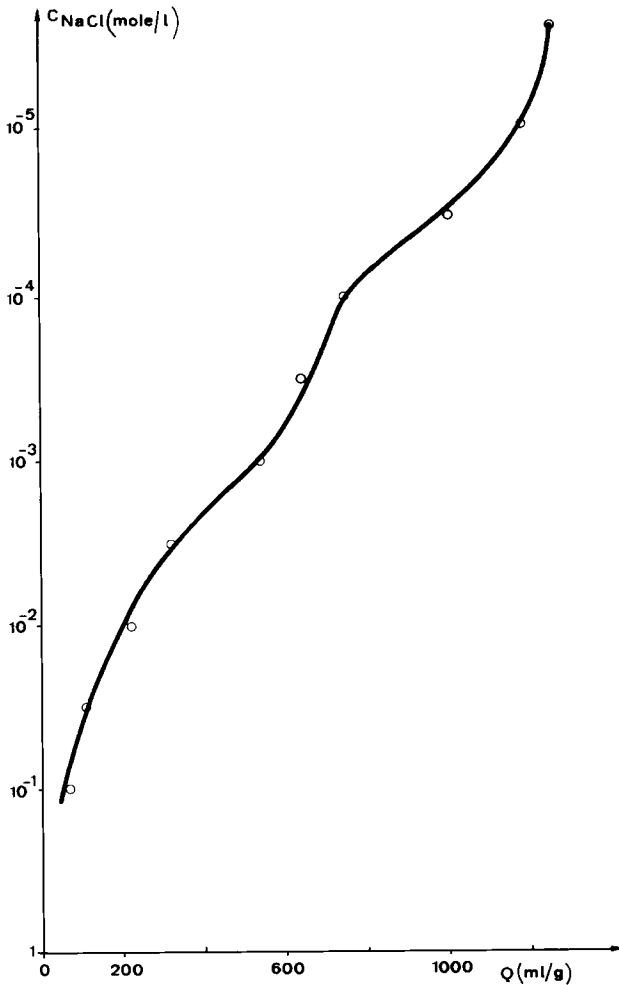


Fig. 15. Absorbency of a starch graft polyacrylamide-CMA as a function of NaCl concentration (CMA content 36%).

$0.632Q_e$, when $t = \tau$. τ values were calculated from the swelling kinetics curves $Q = f(t)$ and showed a minimum value at intermediate crosslink density (Table III).

Spherical gels cannot be obtained by grafting vinylic monomers onto starch and the characteristic times τ given here cannot fit the model described by Candau et al. in the later stage of the swelling process; they give a qualitative influence of the crosslink density on the swelling kinetics. A copolymer with a low crosslink density seems to be characterized by a high swelling. When the crosslink density of the gel increases, τ decreases, indicating a faster swelling. No correlation was obtained between the ionic content of the gels and the Q and τ parameters (Table III).

Table III gives also evidence as reported above that the swelling of the cationic gels increases to a maximum as the ionic content increases.

τ values were also determined for a series of hydrolyzed starch polyacry-

TABLE III
Influence of the Crosslink Density and of the Ionic Content on the Swelling
Characteristic Time τ and on the Swelling of Cationic Absorbent

(Crosslink/monomer) $\times 10^3$	% CMA (mol)	Q (mL/g)	τ (s)
4.80	27.8	90	570
1.90	27.8	200	35
1.28	27.8	300	120
0.95	27.8	300	460
0.64	27.8	370	550
0.64	0.0	50	85
0.64	11.0	180	110
0.64	19.0	330	90
0.64	44.0	120	2100
0.64	55.0	80	1250

TABLE IV
Influence of the OH⁻/AN Ratio on the Swelling Characteristic Time τ and on the Maximum
of Swelling of Hydrolyzed Starch Polyacrylonitrile Gels

OH ⁻ /AN	Q _e (mL/g)	τ (s)
1.10	270	290
1.30	360	310
1.65	570	300
1.85	510	460
2.05	360	480

lonitrile (Table IV). An increase of the OH⁻/AN ratio induces changes in the maximum of swelling and in τ value, which are a complicated combination of the crosslink density, the ionic content, and the percentage of soluble chains.

CONCLUSION

The swelling behavior of starch graft anionic and cationic absorbents is related to their structure, their chemical composition, and the nature of solvent. Both types of absorbent have a high water retention and a fast rate of absorption which depend on the crosslink density and on the ionization degree. As expected, the swelling decreases with increasing crosslink density but the rate becomes faster. The expansion of the network is promoted by the charge containing chains. However, an excess of charges results in a swelling decrease. This behavior is explained in terms of counterion condensation and screening effect.

For hydrolyzed starch graft polyacrylonitrile the crosslink density and the ionic content are determined by the hydrolysis conditions. The water retention depends also strongly on the molar weight of the graft polyacrylonitrile. This parameter is correlated to the starch composition. The starch-based absorbent with high amylopectin content has the greatest retention.

The addition of salts results in a continuous swelling decrease for both types of absorbent. But differences in their swelling behavior are observed.

For a given ionic strength, the absorbency of anionic absorbent in presence of solution containing multivalent salts decreases strongly by comparison with NaCl solution. On the other hand, the deswelling of cationic absorbent is less sensitive to multivalent ion effects.

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