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PREPARATION OF STARCH GRAFT COPOLYMERS: INFLUENCE OF SEVERAL PARAMETERS ON STRUCTURE AND PROPERTIES

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ABSTRACT

Samples of starch-*g*-polyacrylonitrile were prepared using the Ce^{4+} ion as initiator. We discuss the influence of the origin of the starch on the polyacrylonitrile content of the copolymer, on the frequency of the grafted chains, and on the molecular weight of the graft. Relations between alkaline hydrolysis conditions and liquid absorption were also studied. The retention increases with the molecular weight of the grafted polyacrylonitrile, and this factor depends on the origin of the starch. Higher absorptions were obtained with low amylose content samples. An absorption maximum was observed that depends on the time of hydrolysis and consequently on the carboxylate group content.

INTRODUCTION

Materials with enhanced water sorption capacity are obtained when charged sites are placed along loosely crosslinked chains. The electrostatic repulsions between ionic sites promote a large expansion of the network. In water, these gels are characterized by fast uptake of water and high retention. Therefore, they have been patented for many original industrial applications (disposable hygienic items, agriculture, etc.) [1, 2].

Graft polymerization of acrylonitrile onto starch and hydrolysis of the re-

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sulting copolymer with alkali (to convert the nitrile groups to amide and alkali metal carboxylate groups) lead to a material which forms a gel in aqueous solution and is a very good water retainer. It can absorb up to 2000 g of distilled water per gram of dry gel. However, in salt solution the ionic charges are screened by the counterions of the salt, and the amount of liquid absorbed by the gel decreases by a factor of 10 to 100. Hydrogels from starch are used as thickeners for aqueous systems, water retainers, and flocculants. Cellulose water retainers have also been made by direct grafting of polyacrylic acid onto cellulose [3, 4].

In this work, samples of starch-*g*-polyacrylonitrile have been prepared with the Ce^{4+} ion as initiator. Various parameters affect the grafting and saponification reactions, and consequently modify the gel absorbency. We here examine the origin of the formation of a covalent gel by grafting an acrylic polymer onto starch, and we study the influence of the origin of the starch on the characteristics of the grafted material on swelling after hydrolysis.

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EXPERIMENTAL

Materials

Starches from different sources were obtained from several suppliers (Roquette, Doittau, and Merck). Acrylonitrile (AN) (Prolabo), acrylic acid (AA) (Prolabo), and acrylamide (AM) (Fluka) were commercial products.

Titration of Amylose

Starch can be found in most higher plants and is a granule composed of linear and branched macromolecules: amylose, amylopectin, and an intermediate fraction that is less branched than amylopectin [5-7]. Amylose is a linear chain formed with *α-D*-glucopyranosyl units linked (1→4) and has an helicoidal conformation. Its average molecular weight is between 2×10^4 and 10^6. Amylopectin is highly branched with *α-D*-glucopyranosyl units linked (1→4) and (1→6) and has a molecular weight over 10^7.

The amylose content of starches depends on the source. It was determined by an amperometric method [8] based on the high absorption capacity of amylose for iodine (20%), while iodine is poorly bound to amylopectin (0.5%). Iodine was liberated by titrating with standard potassium iodate into an acid solution containing starch and potassium iodide. The amperometric current depends on the free iodine concentration. After a small initial increase, there is little change in the free iodine concentration until the amylose has been saturated with iodine. Amylose AVEBE was assumed pure and taken as reference.

Starch samples (100 mg) were dissolved in 10 mL of 1 *N* KOH. This solution was then neutralized by the addition of 1 *N* HCl. Potassium iodide was introduced and, after dilution, the concentration of KCl and KI was adjusted to 0.05 *N*. Air was expelled with argon, and the titration was carried out on a Tacussel instrument by the addition of 5 m*M* KIO_3. A 10-mV potential was applied between 2 platinum electrodes, and the current, due to the iodine formed *in situ*, was plotted against the titer.

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Synthesis of Starch Graft Copolymers

To a 250-mL reactor were added 5 g starch and 83 mL H_2O. The slurry was stirred and heated at 85°C for 60 min under nitrogen. After cooling to 30°C, 7.5 g acrylonitrile was added, and the slurry was stirred for 5 min before adding the initiator (170 mg $Ce(NH_4)_2(NO_3)_6$ in 1.5 mL of 1 *N* HNO_3). The mixture was kept at 30°C for 2 h, then 100 mL ethanol was added, and the pH was adjusted to 6.5 with 1 *N* NaOH. The polymer was filtered and first washed with a 50/50 water-ethanol mixture and then with ethanol. The product was dried under reduced pressure at 60°C.

The percentage of homopolymer was calculated from the amount of homopolymer separated by Soxhlet extraction with an appropriate solvent. DMF/acetic acid mixture, water, acetone, and DMF, respectively, were used to dissolve polyacrylamide, polyacrylic acid, poly(methyl methacrylate), and polyacrylonitrile.

Characterization of Polyacrylonitrile-Grafted Starch

The starch grafted with polyacrylonitrile was characterized by weight gain, elemental microanalysis, and molecular weight of the polyacrylonitrile obtained after acid degradation of the starch.

Banks et al. [9] showed that amylose can be entirely degraded into maltose units by heating in 0.75 *M* H_2SO_4 at 100°C for 2 h. Complete degradation of amylopectin is difficult. The following experimental procedure is given as an example. One gram of grafted sample was added to 80 mL of 0.5 *N* HCl, and the slurry was refluxed for 2 h. The mixture was filtered, washed successively with water and methanol, and then dried. After hydrolysis the polymer did not show any IR band characteristic of the glucose unit of the polysaccharide chain.

Grafted PAN Molecular Weight

After starch hydrolysis, the intrinsic viscosity of polyacrylonitrile was determined in DMF at 25°C, and the average molecular weight was calculated from Onyon's relation [10]. PAN must be carefully dissolved because microgel can form when traces of water are present in DMF. The following procedure was used: 12.5 mg of sample was added to 20 mL of DMF and the solution was stirred for 24 h at room temperature, then heated at 70°C for 2 h. The solution was kept at room temperature for another 24 h, and the procedure was repeated until no microgel could be observed.

Alkaline Hydrolysis

To a 50-mL reactor, 500 mg of grafted starch and 20 mL of 0.5 *N* NaOH were added. The mixture was heated to 90-95°C and a red to yellow color appeared. When the color had faded, the reaction was stopped by precipitation in MeOH. The product was filtered and dried under vacuum at 40°C.

Gel Characterization

Gels were characterized by elemental microanalysis and potentiometric titration. Samples were passed through a 100-200 μm sieve and swollen in water before adding an excess of NaOH (pH 11) and titrated by the slow addition of HCl. The results obtained by both methods were in good agreement. They are given as the percentage of acrylate monomer unit.

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RESULTS AND DISCUSSION

Depending on the type of starch, the weight gain was 48-54%. The lower percentage observed for amylose AVEBE can be attributed to degradation occurring during cooling of the slurry after the gelatinization step.

The copolymers are characterized by two parameters that have an important influence on the swelling of the hydrolyzed materials: the graft frequency that gives the number of polyholoside units between two grafting points and the molecular weight of the graft. Several authors have shown that the graft characteristics depend on the origin and the physical state of the starch [11-13]. Hence, the graft copolymerization was carried out with several starches to prepare materials with different structures. Samples of high amylose content (amylose AVEBE and amylomaize) lead to copolymers characterized by lower molecular weight of the graft and more grafting points

TABLE 1. Influence of Amylose Content on Molecular Weight of Grafted Polyacrylonitrile

Starch origin	Amylose,[a] %	Conversion, %	Weight gain, %	$M_n \times 10^{-3}$ [b]	Graft frequency
Waxy corn	0.5	75	52.5	870	4950
Manioc	18	80	54.5	865	4750
Potato	20	76	53.0	915	4700
Merck	25	91	57.5	525	3000
Corn	25	53	44.5	840	5650
Wheat	27	77	53.5	670	4150
Amylomaize	68	65	49.5	410	2250
Amylose AVEBE	100	62	42.0	310	2850

[a] Determined by amperometric titration of iodine.

[b] Determined by viscosity of polyacrylonitrile in DMF at 25°C.

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on the polysaccharide chain compared to other starches in which amylopectin is the major component (Table 1). The differences between the samples of high amylopectin content are attributed to differences in their structure (presence of intermediate material, short chains).

Grafting PAN was also carried out on various mixtures of amylose and waxy corn (Table 2). The same dependence was observed, i.e., increasing molecular weight of the graft and increasing graft frequency with increasing amylopectin content of the starch.

To study the influence of the polysaccharide chain length on the characteristic of the grafted copolymer, the graft polymerization of PAN was also carried out with several maltodextrins and dextrans. With increasing degree of polymerization (DP) of the polysaccharide, the percentage of grafted PAN on the polysaccharide chains and the number of graft points decrease, but the molecular weight of the graft increases (Table 3).

Alkaline Hydrolysis

The alkaline hydrolysis of polyacrylonitrile at 80-100°C, which converts the nitrile group into a mixture of amide and carboxylate, has been the sub-

TABLE 2. Influence of the Composition of Starch Mixtures on the Graft Copolymerization[a]

Amylose AVEBE, %	Waxy corn, %	Conversion, %	Grafted PAN, %	$\bar{M}_n \times 10^{-3}$	Graft frequency
0	100	75	52	870	4950
25	75	75	50	670	4200
50	50	50	50	550	3300
75	25	50	50	510	3150
100	0	60	40	310	2850

[a] Experimental conditions: 31 m*M* AGU, 0.14 *M* AN, 0.31 m*M* Ce^{4+}, 0.6 m*M* H_3O^+, 83 mL H_2O, $T = 25°C$, reaction time 2 h.

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TABLE 3. Influence of the Polymerization Degree of the Polysaccharide on the Graft Characteristics

	$\overline{DP}$	Grafted, %	$\bar{M}_n \times 10^{-3}$	Graft frequency
Maltodextrine	20	85	120	140
Maltodextrine	50	85	140	150
Maltodextrine	100	80	170	240
Dextrane	37	70	190	450
Dextrane	1120	50	500	3200
Amylose AVEBE	2600	40	300	2850

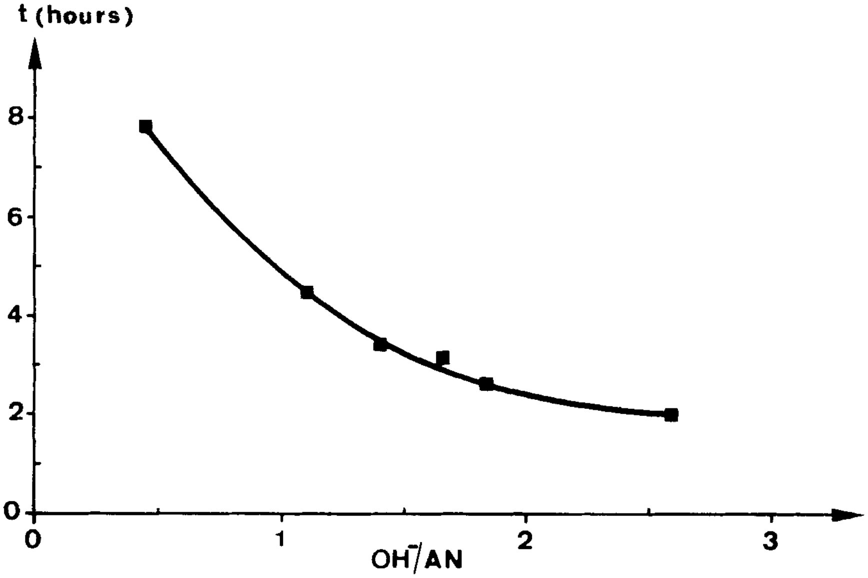

FIG. 1. Starch-*g*-polyacrylonitrile hydrolysis. Discoloration time versus base/acrylonitrile ratio.

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ject of a number of publications [14-17]. Intermediate colored products are formed. The coloration was attributed by Grassie to the formation of partly hydrogenated naphtiridine-type structures, which is initiated by the nucleophilic attack of OH^- on the carbon atom of the nitrile group. Crosslinking is known to occur during this step. The end of the reaction is characterized by the light yellow color of the solution, indicating the disappearance of the conjugated system $\lbrack CH{=}N \rbrack_n$ and the formation of $CONH_2$ and CO_2^- groups.

The saponification of polyacrylonitrile-grafted starch yields an ionic gel, the macroscopic properties of which depend on the characteristics of the graft and on the experimental conditions. Therefore, the following parameters were studied: (a) base/acrylonitrile ratio, (b) hydrolysis time, and (c) molecular weight of the grafts. According to Fanta et al. [18], reaction was assumed to be complete when the discoloration of the orange-red solution had occurred. Figure 1 shows that the rate of discoloration increases with the OH^-/acrylonitrile ratio. However, the percentage of soluble material increases with this ratio (Fig. 2), indicating some destruction of the gel either by scission of cross-

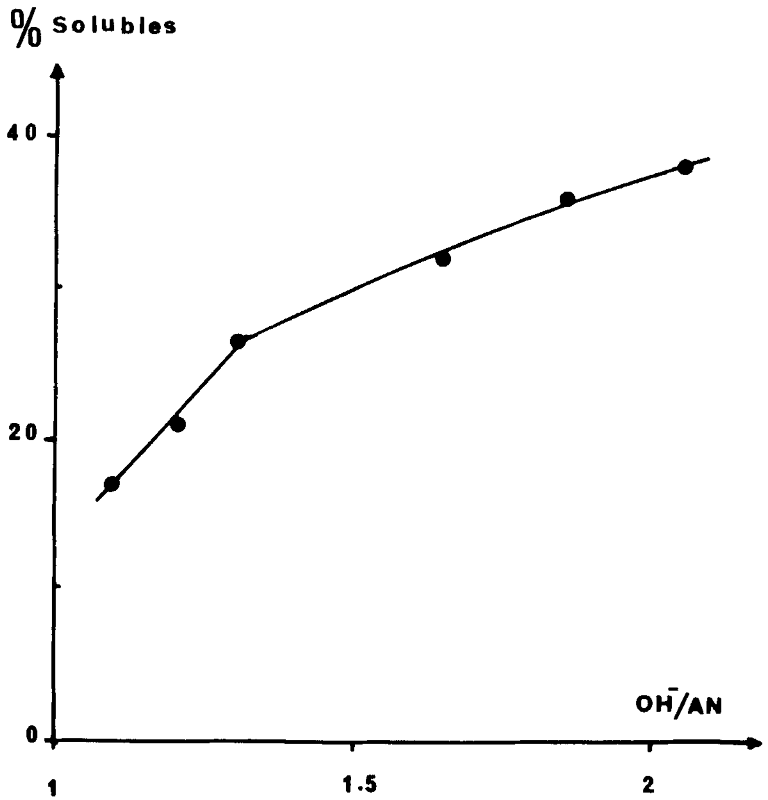

FIG. 2. Starch-*g*-polyacrylonitrile hydrolysis reaction. Dependence of solubles on the base/acrylonitrile ratio.

links or by chain cleavage. The percentage of acrylate units first increases with time and then drops after 5 h (Fig. 3). This behavior can be attributed either to decarboxylation reactions or to chain solubilization due to the hydrolysis conditions.

The gel structure is particularly sensitive to the experimental conditions during the hydrolysis step and, consequently, the water sorption of the gel, which depends on the number of crosslinks and on the ionic content, will be influenced by the hydrolysis reaction. The variation of gel swelling with the base concentration is shown in Fig. 4.

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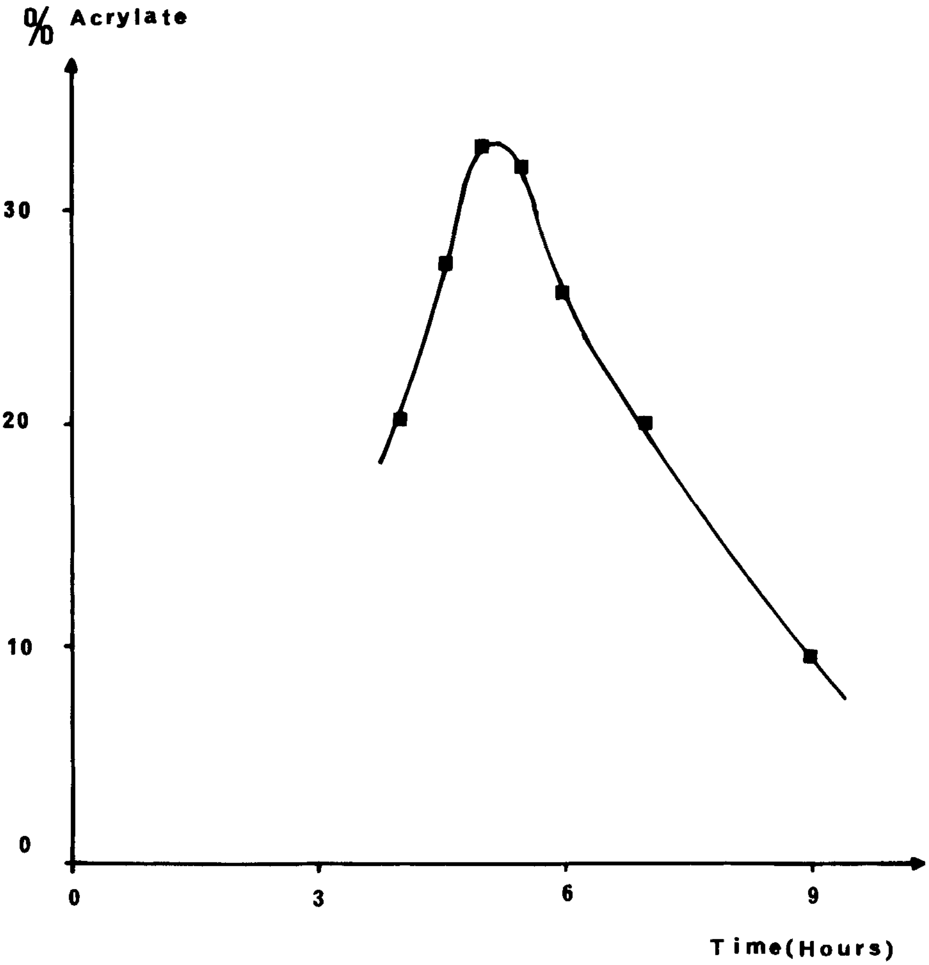

FIG. 3. Percentage acrylate groups formed as a function of the hydrolysis reaction time.

The water absorbency of this type of "superabsorbent," containing starch, also depends strongly on the amylose content (Table 4). High-amylopectin starches lead to hydrogels containing grafts with high molecular weight and having greater retention.

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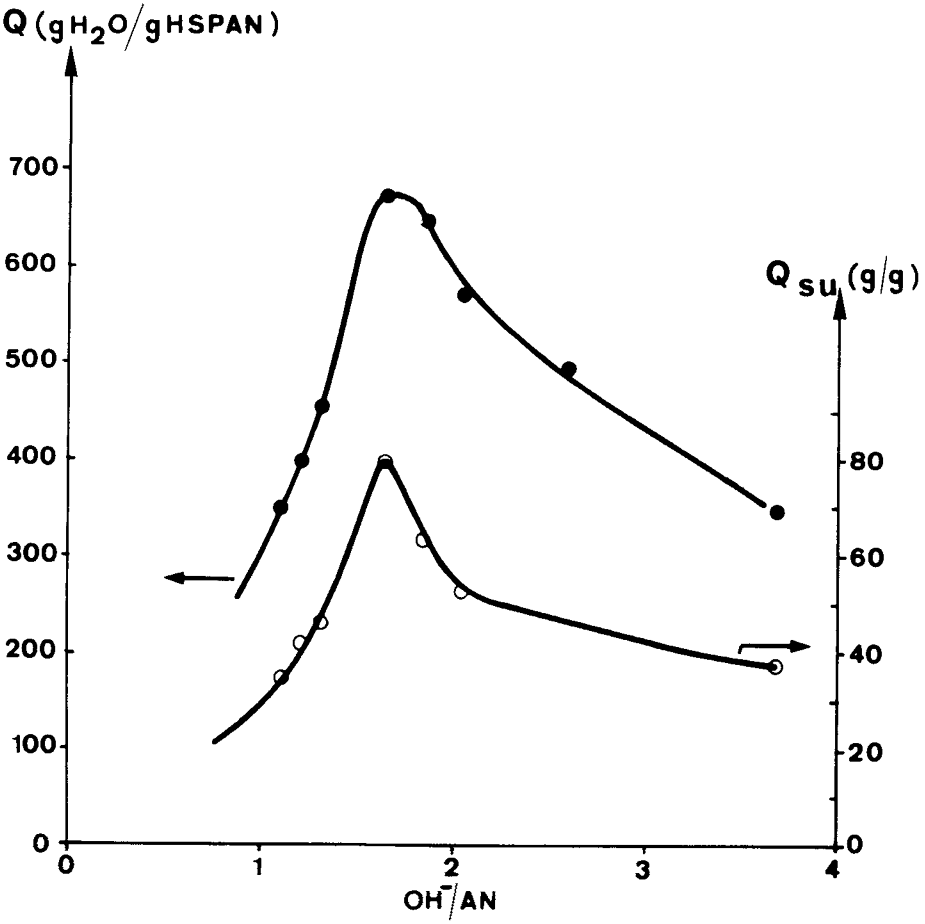

FIG. 4. Water retention (Q) and synthetic urine retention (Q_{su}) versus alkali/acrylonitrile ratio during hydrolysis.

CONCLUSION

In starch-*g*-polyacrylonitrile "superabsorbents," the crosslink density and the ionic unit content are determined during the hydrolysis reaction and are dependent on the experimental parameters. Gel formation derives from the chemical

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TABLE 4. Absorbency of Hydrolyzed Starch-*g*-Polyacrylonitrile versus Starch Origin[a]

Starch origin	Amylose, %	$\bar{M}_n \times 10^{-3}$, PAN	Acrylate, %	Swelling, g/g
Waxy corn	0.5	870	36	1150
Manioc	18	860	31	1550
Potato	20	900	39	1250
Corn	25	840	29	1300
Wheat	27	670	22	900
Amylomaize	65	400	32	400
Amylose AVEBE	100	300	34	300
Starch, Merck	25	500	35	700

[a] Experimental conditions: 300 mg starch-*g*-PAN are hydrolyzed by 12 mL 0.35 *N* NaOH at 90-95°C for 165 min.

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crosslinking occurring during the saponification reaction. The base reacts by nucleophilic attack on the nitrile group, leading to interchain crosslink propagation. It has been found that the water sorption capacities of the gels depend on the base concentration and on the reaction time. The water retention increases with the content of ionic units in the gel. However, depending on the hydrolysis parameters, chain cleavage can occur, decreasing water sorption. The number and length of polyacrylonitrile chains grafted onto the polysaccharide depend on the amylose content of the starch. Highly branched amylopectin promotes a graft with high molecular weight. This structural parameter accounts for the high retention capacity obtained with "superabsorbent" prepared from waxy corn.

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