

Modified Chitosan. II. H-ChitoPAN, a Novel pH-Responsive Superabsorbent Hydrogel

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ABSTRACT: Chitosan was modified with polyacrylonitrile (PAN) through ceric-initiated graft copolymerization. The chitosan-g-PAN product was saponified using sodium hydroxide aqueous solution to prepare a novel superabsorbent hydrogel, H-chitoPAN. Duration of completing the saponification reaction as well as the water absorbency capacity of the hydrogel was decreased with increasing the alkaline concentration. Either chitosan-g-PAN or H-chitoPAN was characterized by FTIR spectroscopy and DSC, TGA, and DTG thermal methods. According to FTIR, all the nitrile groups were converted to carboxylate and carboxamide groups. Both modified chitosans exhibited enhanced thermal stability over chitosan. The H-chitoPAN superab-

sorbent hydrogel was recognized to be highly responsive to pH. Study of net effect of H⁺/OH⁻ concentration (in absent of buffer solution) showed several sharp and large volume changes vs small pH variation in the range of 2–13. This abrupt swelling behavior was explained based on variety of pH-dependent interactions of functional groups incorporated in the gel network by an external pH modulation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3115–3121, 2003

Key words: hydrogels; polysaccharide; radical polymerization; swelling; graft copolymer

INTRODUCTION

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents. They are mainly used in sanitary goods for absorbing the body fluids and in soil conditioning and improving water retention capability of soil in agriculture and horticulture.¹ They are also found to be valuable in some specialized applications, including controlled delivery of bioactive agents. Specifically engineered hydrogels may act intelligently, i.e., respond with large changes to small physical or chemical stimuli such as temperature and pH. These responsive or smart hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology.^{2,3}

Superabsorbing resins were first developed with a view to utilizing agricultural materials, and are typified by the hydrolyzed corn starch-g-poly(acrylonitrile), H-SPAN.^{4,5} Since then, starches from different resources⁵ as well as other polysaccharides, for example, cellulose,^{6,7} hydroxyethyl cellulose,^{8,9} agar,⁴ sodium alginate,^{10,11} and guar gum¹² were graft copoly-

merized to achieve water absorbing polymers. Polyacrylonitrile (PAN), polyacryamide, and poly(acrylic acid)¹³ have been frequently grafted, mostly onto starch, using different initiators especially the ceric-saccharide redox system.¹⁴

Chitosan is an aminopolysaccharide produced from chitin, the most abundant biomass in the world. Its potential applications range from biomedicine and pharmacy to water treatment.¹⁵ Optimized grafting of PAN onto chitosan was reported in a previous article.¹⁶ In this article, we report synthesis and characterization of a novel chitosan-based ampholytic superabsorbing hydrogel that sharply responds to pH changes in either acidic or basic conditions.

EXPERIMENTAL

H-ChitoPAN synthesis

Chitin was extracted from shrimp shell and then deacetylated to chitosan with degree of deacetylation of 0.76.¹⁶ Graft copolymerization of acrylonitrile onto chitosan was carried out under argon using ceric ammonium nitrate (CAN, from Merck) as an initiator. Thus, in a 50-mL flask, chitosan (0.20 g) was dissolved in degassed distilled water containing 2 wt % of acetic acid. To control the reaction temperature, the flask was placed in a water bath preset at desired temperature. Acrylonitrile (1.60 g) (AN, Merck) was added to the flask and the mixture was heated at 50°C and

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stirred for 5 min. Then the initiator solution (0.006 M CAN in 1 N HNO₃) was added to the mixture. The mixture was continuously stirred until completion of the reaction (2 h). The product was then precipitated by neutralization using 1 N NaOH solution. It was thoroughly washed with methanol and dried at 50°C for 1 h. The crude product was Soxhlet-extracted with dimethylformamide (24 h) to separate the PAN homopolymer.

The chitosan-g-PAN (grafting percentage 230%, add-on value 70%) was saponified using 20 mL aqueous sodium hydroxide, NaOH, solution with given concentration. Thus, in a loosely stoppered 100-mL flask, 0.50 g of the chitosan-g-PAN powder was dispersed and gently stirred in the base solution at room temperature under atmospheric conditions (5 min). Then the dispersion was heated at 110–120°C with magnetic stirring. The saponification was continued until the color of the mixture changed from deep orange-red to light yellow. Time of the discoloration, depending on the base concentration, varied from 35 to 140 min. The pasty mixture was allowed to cool to room temperature and neutralized to pH 7.0 by addition of 10 wt % aqueous acetic acid solution. Methanol (200 mL) was added to the gelled product while stirring. After a few minutes, the H-chitoPAN light yellow precipitate was filtered, washed with fresh methanol (2 × 50 mL), and dried at 30°C for 3 h.

Infrared spectroscopy

IR spectra of samples were taken in KBr pellets using a Unicam Mattson-1000 FTIR spectrophotometer.

Absorbency measurements

A H-chitoPAN sample (0.05 g) was put into a weighed teabag and immersed in 100 mL distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the teabag from water and hanging until no drop drained (~20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency was calculated using the following equation:

$$\text{Absorbency} = (W_s - W_d)/W_d \quad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was ±3%.

Absorbency at various pHs

In this series of experiments, each individual solution pH was obtained by dilution of aqueous NaOH (pH 13.0) or HCl (pH 2.0) solutions to achieve pH ≥ 6 and

pH < 6, respectively. The pH values were precisely checked by a pH meter (Metrohm/620, accuracy ±0.1). Then, 0.10 g of the dried H-chitoPAN sample was used for the swelling measurements (equilibrium swelling time 3 h).

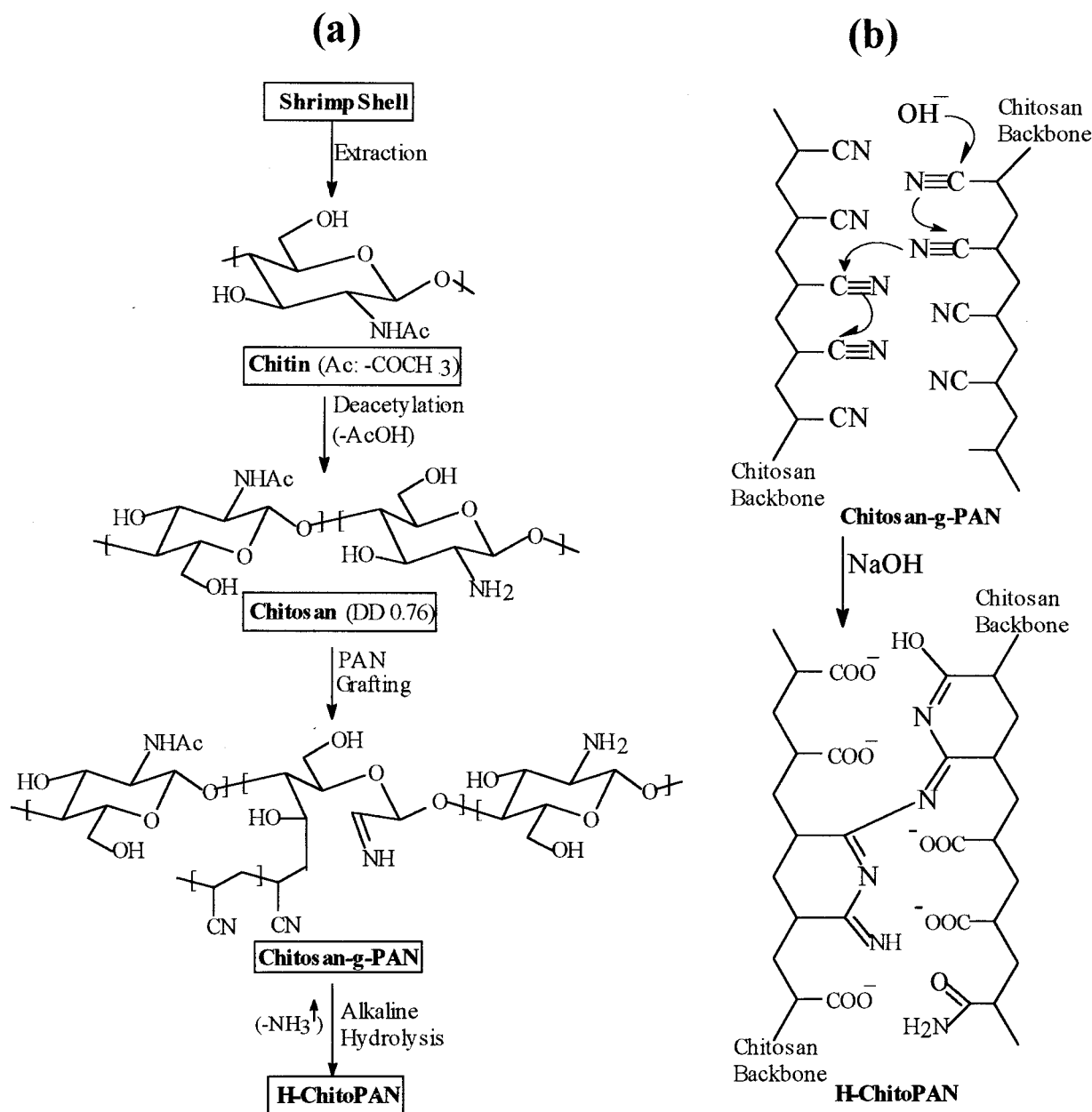
Thermal analysis

A simultaneous thermal analyzer (STA-625, Reometric Scientific) was used for differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen. The heating rate was 20°C/min.

RESULTS AND DISCUSSION

Synthesis and spectral characterization

Poly(acrylonitrile), PAN, was grafted onto chitosan in a homogenous medium using a ceric initiator under inert atmosphere. This copolymerization system has already been optimized.¹⁶ The chitosan-g-PAN copolymer was then hydrolyzed with NaOH solution to produce a new superabsorbent resin, H-chitoPAN (Scheme 1). During the saponification, NH₃ gas evolves and a deep red color develops due to intermediate formation of naphthyridine cyclic structures (including imine, —C=N—, conjugated bonds) from adjacent nitrile groups.^{5,17} Some crosslinks may form if the mentioned reaction occurs between adjacent PAN pendant chains. The intermediate heterocycles are subsequently hydrolyzed with a resulting color change from red to light yellow. This sharp color change was used as an indication to halt the alkaline treatment. Infrared absorption analysis of H-chitoPAN shows no nitrile functionality in comparison to the initial chitosan-g-PAN [Fig. 1(b) and (c)]. Instead, as is clear from Figure 1(c), the H-chitoPAN superabsorbent product comprises a chitosan backbone with side chains that carry mainly sodium carboxylate (and rarely carboxamide) functional groups that are evidenced by a new intense peak at 1560–1600 cm⁻¹. (The shoulder at ~1690 cm⁻¹ and sharp peak at ~1676 cm⁻¹ are attributed to amide and absorbed moisture, respectively). The very intense characteristic band at 1569 cm⁻¹ is due to C—O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1407 cm⁻¹, which is related to the symmetric stretching mode of the carboxylate anion.¹⁷ Combination of absorption of the carboxylate and alcoholic O—H stretching bands appeared in the wide range of 3500–2550 cm⁻¹. Incompletely hydrolyzed structures may also give rise to a few crosslinking points resulting in a loosely crosslinked copolymeric network. In the case of H-SPAN, a maximum conversion of 70% of nitrile to carboxyl groups has been reported, and the remaining 30% are amide groups.¹⁸ In the case of H-chitoPAN, we are trying to determine



Scheme 1 (a) Synthetic pathway to H-chitoPAN hydrogel, (b) a brief mechanism for the last step (alkaline hydrolysis).

the amide/acid ratio. However, we realized that precise control of the ratio is practically impossible. In fact, details of the chemical processes and mechanisms involved in the H-SPAN formation are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors, for example, hydrogen bonding of neighboring amide and carboxyl groups.¹⁸ Weaver et al.¹⁹ suggested that condensation may also occur between carboxyl and amide groups to form imide structures.

Effect of NaOH concentration

The alkaline hydrolysis of chitosan-g-PAN was performed using different concentrations of the hydroxyl ion, ranged from 0.5 to 2.0 N. It was found that the saponification mixture was discolored faster at a higher NaOH concentration (Fig. 2). In addition, lower absorbency was achieved when a higher concentration of the base was applied. This may be attributed to formation of more crosslinks at higher OH⁻ concentration. It is a well-known rule in all of hydrogels that a small increase in degree of crosslinking causes an appreciable decrease in swelling capacity.²⁰ In our case, higher hydroxyl ion concentration results in the higher extent of the reactions between nitrile groups including those of adjacent pendant PAN grafts of the neighboring copolymer chains [Scheme 1(b)]. As a result, formation of more crosslinks leads to lower swelling ca-

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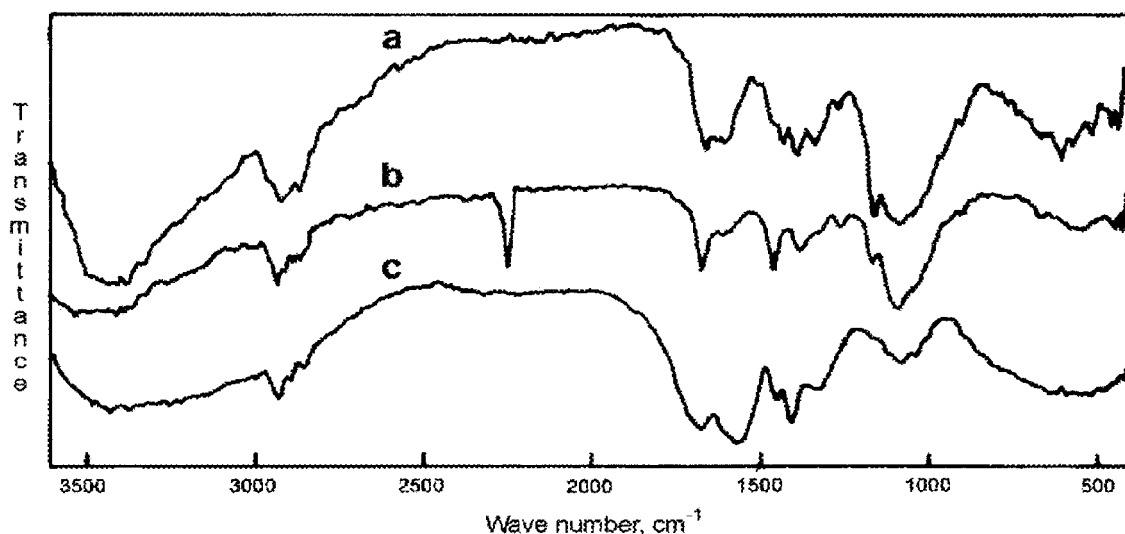


Figure 1 FTIR spectra of (a) chitosan, (b) chitosan-g-PAN, and (c) H-chitoPAN superabsorbent hydrogel.

capacity. A similar observation has been reported by Castel et al.²¹ in the case of the hydrolysis of starch-g-PAN.

Effect of pH on equilibrium swelling

The equilibrium swelling (ultimate absorbency) of the H-chitoPAN hydrogel was studied at various pHs ranged from 2.0 to 13.0 (Fig. 3). No additional ions (through buffer solution) were added to medium for

setting pH because absorbency of a superabsorbent is strongly affected by ionic strength.²⁰ In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and pK_a).³ Therefore, stock NaOH (pH 13.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

Three distinct levels of absorbency are obvious from the Figure 3. There are 220, 150, and 20 g/g, where each comprises different states of the polyampholytic network. Various phenomenon involved in the swelling behavior of the hydrogel are tabulated in Table I.

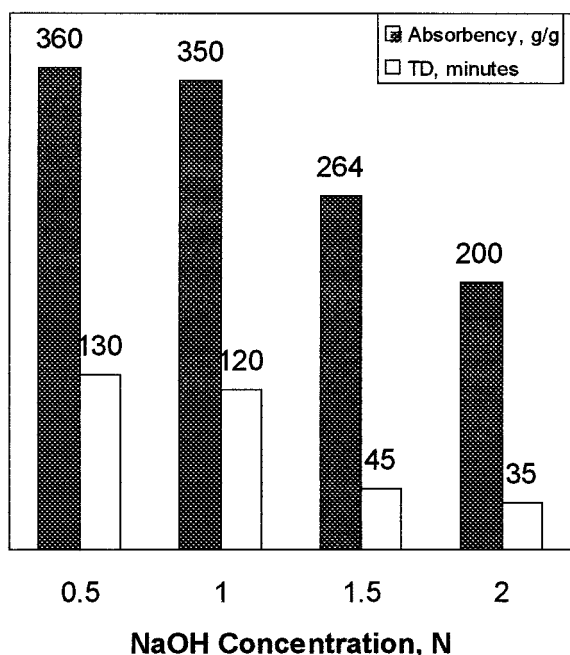


Figure 2 Effect of concentration of the NaOH solution (used for the hydrolysis of chitosan-g-PAN) on the time of discoloration of the saponification mixture (TD) and on the water-absorbency of the H-chitoPAN superabsorbent product.

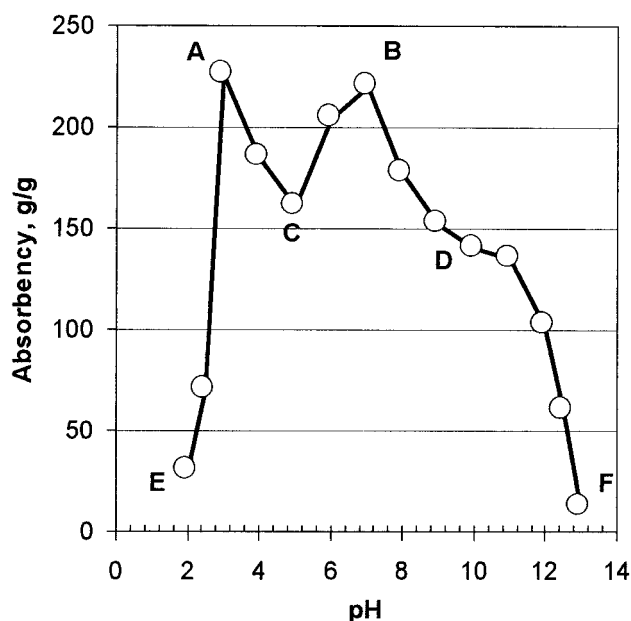


Figure 3 Water-absorbency dependence of H-chitoPAN superabsorbent on pH.

TABLE I
The Main Species and Interactions Affecting the Swelling Behavior of H-chitoPAN Superabsorbent Hydrogel at Different pHs

pH	Main interacting species	Main interaction affecting on swelling
≤2	NH ₃ ⁺ Cl ⁻ , COOH	Screening effect by excess Cl ⁻ ions
2–3	NH ₃ ⁺ Cl ⁻ , COOH	Intense repulsion of NH ₃ ⁺ -NH ₃ ⁺
3–4	NH ₃ ⁺ Cl ⁻ , COOH	Repulsion of NH ₃ ⁺ -NH ₃ ⁺
4–6	NH ₂ , COOH NH ₃ ⁺ COO ⁻	NH ₂ -COOH interchain hydrogen bonding NH ₃ ⁺ -COO ⁻ interchain attraction
6–8	NH ₂ , COO ⁻ Na ⁺	Intense repulsion of COO ⁻ -COO ⁻
8–11	NH ₂ , COO ⁻ Na ⁺	COO ⁻ -COO ⁻ repulsion weakened by Na ⁺ screening effect
>11	NH ₂ , COO ⁻ Na ⁺	Strong screening effect by excess Na ⁺ ions

Under acidic conditions, the swelling behavior is controlled mainly by amino group (NH₂) on the C-2 carbon of the chitosan component. It is a weak base with an intrinsic pK_a of about 6.5,²² so it gets protonated and increased charge density on the polymer should enhance the osmotic pressure inside the gel particles because of the NH₃⁺-NH₃⁺ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the gel (point A, Fig. 3). However, at very acidic conditions (pH ≤ 2), a screening effect of the counter ions, i.e., Cl⁻, shields the charge of the ammonium cations and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). Around pH 5, the carboxylic acid component comes into action as well. Because the pK_a of the weak polyacid is about 6.4,²³ its ionization occurring above this value may favor enhancing absorbency. But under pH 6.4, at a certain pH range 4–6 (point C, Fig. 3), the majority of the base and acid groups are as nonionized forms, so hydrogen bonding between amine and carboxylic acid (and probable carboxamide groups) may lead to a kind of crosslinking followed by a decreased swelling. A similar observation is recently reported in the case of an interpenetrating network composed of poly(*N*-isopropylacrylamide)-poly(acrylic acid).²⁴ At higher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO⁻) causes increasing in swelling. Again, a screening effect of the counterions (Na⁺) limits the swelling at pH 8–11 and opposed the swelling at pH > 12, so that the hydrogel totally collapses at pH 13. Such behavior has been reported for copolymeric gels from acrylic acid (the anionic constituent) and methacrylamidopropyl trimethyl ammonium chloride (the cationic constituent).³ In this system, a combination of attractive or repulsive electrostatic interactions and hydrogen bonding have been recognized to be the main reason for existence of several phases observed in various environmental conditions.

Thermal characterization

DSC and TGA traces are presented in Figure 4. The initial chitosan exhibits two distinct weight losses in its thermogravimetric curve. The one in the range of 40–168°C, peaking at 90.9°C, is associated with loss of water (6.6 wt %), and the other in the range 270–363°C, with maximum decomposition rate at 325°C, has been ascribed elsewhere.²⁵ Grafting of acrylonitrile makes the chitosan hydrophobic. A weak endothermic transition in DSC (curve b, 70.5°C) and a little absorbed water in TGA (curve b, the first weight loss

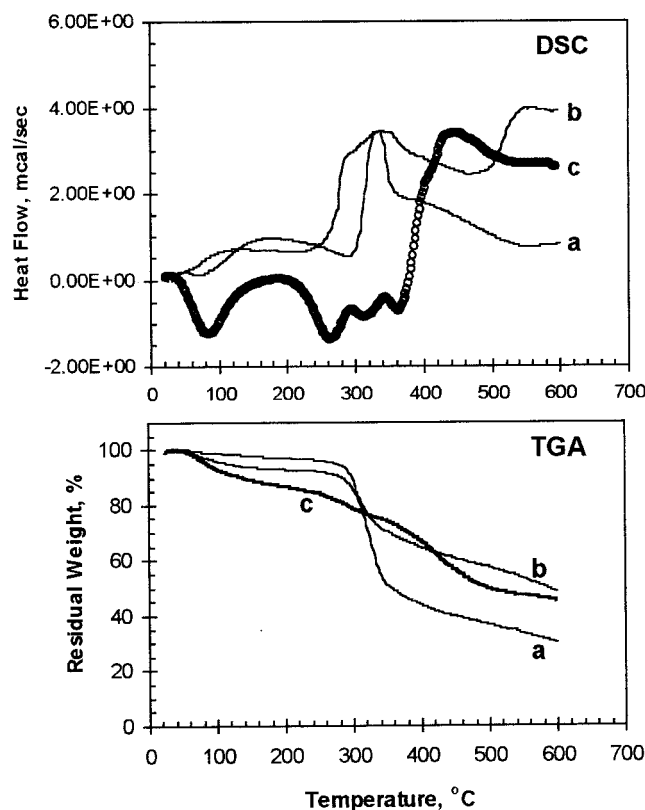


Figure 4 DSC and TGA thermograms of (a) chitosan, (b) chitosan-g-PAN, and (c) H-chitoPAN superabsorbent. Heating rate 20°C/min, under N₂.

TABLE II
Thermal Characteristics of Chitosan and the Modified Chitosans (Heating Rate 20 °C/min under N₂)

Sample	DSC	T_f^b , °C (WL _f ^c)	TGA		
	Temp., °C (ΔH^a , J/g)		Onset, °C	IPDT ^d , °C	Char yield at 600 °C, wt %
Chitosan	70.8 (+33.0) 340.0 (-383.7)	90.9 (6.6%)	293.0	417	30.0
Chitosan-g-PAN	70.5 (Negligible) 338.0 (-752.4)	75.7 (2.5%)	291.3	479	48.3
H-ChitoPAN	90.6 (+119.1) 267.9 (+54.8) 316.8 (+11.5) 375.0 (NM ^e) 454.6 (-71.4)	66.7 (13.2%)	—	448	45.2

^a Enthalpy change, +: endothermic, -: exothermic.

^b Temperature at the first weight loss of the corresponding peak of the DTG curve.

^c The first weight loss, wt %

^d Integral procedural decomposition temperature.

^e Nonmeasurable by the instrument.

2.5 wt %) indicate that the graft copolymer chitosan-g-PAN is much more hydrophobic than the other polymers. Conversely, the H-chitoPAN shows a large amount of absorbed moisture (TGA curve c, 13.2% weight loss; DSC curve c, intense endothermic peak at 90.6°C).

Details of the thermal analysis data are summarized in Table II. IPDT (integral procedural decomposition temperature),²⁶ as a means of summing up the whole shape of the normalized data curve of TGA, was also calculated to get a more semiquantitative data regarding the relative thermal stabilities. Overall, according to the char yield and IPDT values, thermal stability of both grafted and hydrolyzed grafted copolymers is improved in comparison with chitosan itself. It may be attributed to formation of conjugated cyclic systems consisting —C=N— groups from the pyrolytic addition reaction of adjacent nitrile groups²⁷ in the case of chitosan-g-PAN. The important feature of this conjugation is the sudden evolution of a large amount of heat (752.4 J/g). Although there is no nitrile group in H-chitoPAN structure, the existence of COO⁻Na⁺, COOH, and CONH₂ groups improve its thermal stability (IPDT 448°C) over chitosan. These various groups of the synthetic part as well as the functional groups of the polysaccharide part, i.e., NH₂, NH₃⁺, NHCOCH₃, and OH, participate in a variety of reactions upon heating. In the DSC cure of the H-chitoPAN superabsorbent, four distinct endothermic peaks are observed. The first peak (ΔH 119.1 J/g) is due to the evaporation of absorbed water in the sample. The second peak (ΔH 54.8 J/g) at temperature 267.9°C may be attributed to evolution of ammonia by the formation of imide group via cyclization.²⁸ The third endothermic peak is probably due to deacetylation of chitosan moieties, because a part of polyacrylic carboxylic groups are forming salt bands with the amino groups of chitosan sections, and therefore are not susceptible to degradation

by dehydration and decarboxylation reactions as normal polyacrylic acids do.²⁹ The fourth endothermic peak (375.0°C) may be related to decarboxylation. The last enthalpy change starts above 400°C and extends to 500°C, with a maximum decomposition rate around 454°C (exothermic, ΔH ~-71.4 J/g). It corresponds mainly to the degradation of the polyacrylic chains and rarely to the decomposition of the rest of the saccharide backbone.

CONCLUSION

H-ChitoPAN, a new superabsorbent hydrogel, was synthesized through saponification of chitosan-g-PAN prepared from grafting of polyacrylonitrile onto chitosan. Both modified chitosans were spectroscopically and thermally characterized. Swelling capacity of the hydrogel was recognized to affect by alkaline (NaOH) concentration, so that lower concentration of NaOH resulted in higher water absorbency. The superabsorbent swelling exhibited a high sensitivity to pH. Study of net effect of H⁺/OH⁻ concentration was carried out at various pHs in absent of any buffer solution. Several sharp and large volume changes were observed vs small pH variations. Ionic repulsion between charged groups incorporated in the gel matrix by an external pH modulation could be assumed as the main driving force responsible for such abrupt swelling changes. This superabsorbent polyampholytic network intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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