

## GRAFT COPOLYMERIZATION OF ACRYLONITRILE ONTO POTATOES STARCH BY CERIC ION

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Graft copolymers of potatoes starch and acrylonitrile were synthesized in aqueous solution by free-radical polymerization using two initiators  $Ce(SO_4)_2$  and ceric ammonium nitrate (CAN). The polymer fractions separated after the grafting reactions were characterized by elemental analysis, Fourier-transform infrared spectroscopy,  $^1H$ -NMR spectroscopy, and DSC. After hydrolysis with NaOH of the grafted fractions, water soluble polymers have been obtained.

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*Keywords:* potatoes starch, acrylonitrile, Fourier-transform infrared spectroscopy,  $^1H$ -NMR spectroscopy, DSC

### 1. Introduction

Chemical grafting is one of the most popular methods for modifying structure and properties of biopolymers. Vinyl grafting onto the polysaccharides improves their life against biodegradation, thermal stability and metal ion binding ability and therefore grafted polysaccharides have a wide range of industrial applications [1-3]. Considerable amount of research has been published on ceric ion initiated graft copolymerization of acrylic monomers onto starch [4-6]. By modification, starch which is a low cost abundantly available renewable biopolymer, may develop properties comparable to synthetic petroleum-based polymers [7,8]. Native starch granules are water insoluble containing two major polymers: amylose, which is an essentially linear polymer of  $\alpha$ -(1-4-linked-D-glucopyranosyl) units, with few  $\alpha$ -(1-6) linkages, having a number average degree of polymerisation ( $DP_n$ ) of 800-4900, and amylopectin, which consists of branched chains of  $\alpha$ -(1-4-linked-D-glucose) and is highly branched with  $\alpha$ -(1-6-linked-D-glucose) bonds, having a  $DP_n$  of 4700-12800 [9]. The content in amylose is 20-25%, depending on botanic origin of starch. Amylose molecules occur in the starch granules as individual molecules interspersed among the amylopectin molecules, in both the crystalline and amorphous regions [10,11]. Separation of the two major components can be carried out by swelling the starch granules in water at about 80 °C, thus starch granules being preserved; in these conditions, the amylose is solved and diffuses out of granules, into the external medium. However, for many applications, the separation of the amylose from the amylopectin is not performed [12-15].

Grafting of acrylonitrile (AN) on starch gives the possibility to perform numerous further chemical reactions and to synthesize new highly-added value materials for various applications, such as: soil conditioners, additives for paper and textiles, adhesives, enhanced oil recovery, sanitary goods, drug delivery systems, etc. [16-18]. While many studies have been devoted to the grafting efficiency and monomer conversion, less attention has been given to the selectivity of grafting on one of the two main components of starch, amylose or amylopectin. Therefore, our objective was to demonstrate the selective grafting of PAN onto one of the two major constituents of the potatoes starch (PS).

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Graft copolymers of starch are usually prepared by chemical initiation, free radicals generated on the starch backbone being centers for attaching the side chains of synthetic homopolymers. The choice of the initiator is usually made between cerium ammonium nitrate (CAN) in HNO<sub>3</sub> [16,19-21] or other initiation systems [22-26]. In our study, the grafting by either Ce(SO<sub>4</sub>)<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> 0.4 M, or CAN in HNO<sub>3</sub> 1N has been compared. The structure of the fractions isolated after the grafting of PAN on PS were identified by elemental analysis, FT-IR and <sup>1</sup>H-NMR spectroscopy.

## 2. Experimental

### 2.1. Materials

Potatoes starch (PS) purchased from Fluka, humidity content < 10%, ash < 0.5%, was used as received. AN has been distilled at about 77 °C and kept at low temperature. Ce(SO<sub>4</sub>)<sub>2</sub> reagent grade was used as received. CAN reagent grade was used as received. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, NaOH, N,N-dimethylformamide (DMF) and methanol were reagent grade and used as received.

### 2.2. Grafting of acrylonitrile on potatoes starch

The synthesis conditions are given in Table 1.

Table 1. Synthesis conditions for the grafting of PAN on PS.

Sample	AN, mol L <sup>-1</sup>	Ce <sup>4+</sup> , mol L <sup>-1</sup> x 10 <sup>3</sup>	Ce <sup>4+</sup> /AGU, 10 <sup>3</sup>	AN/AGU
GPS1 <sup>a</sup>	0.984	2.6	8.11	3.07
GPS2 <sup>a</sup>	0.334	2.6	8.11	1.02
GPS3 <sup>b</sup>	1.885	5.47	17.73	6.11
GPS4 <sup>b</sup>	1.145	5.47	17.73	3.71
GPS5 <sup>b</sup>	0.945	5.47	17.73	2.47

<sup>a</sup> Solution of Ce(SO<sub>4</sub>)<sub>2</sub> 0.02M in H<sub>2</sub>SO<sub>4</sub> 0.4 M;

<sup>b</sup> Solution of CAN in HNO<sub>3</sub> 1 M;

The general code of the grafted copolymers is GPSx, where GPS means grafted PS and x is the number of synthesis. The reaction was carried out in a three necked round-bottom flask equipped with stirrer, condenser, and nitrogen gas-inlet. Gelatinized starch was prepared first by heating the starch dispersion up to 80 °C, about 30 min; after cooling at 27 °C, the appropriate volume of AN was added, under stirring. The calculated volume of Ce(SO<sub>4</sub>)<sub>2</sub> or CAN solution, was added and the reaction mixture has been left for 2 h. In order to separate the grafted and nongrafted fractions of starch, methanol has been used as nonsolvent being added in three portions to the reaction mixture, as follows: (1) 40 mL, stirring 30 min, and filtration, (2) 40 mL, stirring 15 min, and filtration, and (3) 40 mL and filtration. After filtration, the precipitate having the code *a* has been dried at 40 °C, for 48 h. The three portions of methanol used for precipitation have been collected together, and a new fraction of polymer separated, fraction *b*. It was observed that fraction *a* has been completely soluble in DMF, which is the solvent usually used to remove the PAN homopolymer. Therefore, taking into account that the percentage of PAN homopolymer is usually low, it was assumed that fraction *a* represents only the grafted fraction.

### 2.3. Characterization of starch-g-PAN

The elemental analysis were performed by the elemental analyzer CHNS 2400 II Perkin Elmer. The infrared spectra were recorded in the range of 400 – 4000  $\text{cm}^{-1}$  by KBr pellet technique using a Bruker Vertex 70 FTIR spectrometer. Each spectrum was acquired by accumulation of 32 scans with a resolution of 2  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra have been recorded on  $^1\text{H-NMR}$  spectrometer of 400 MHz, Bruker Avance DRX 400. DSC thermograms were obtained using a Pyris Diamond DSC, Perkin Elmer USA. The heating rate was 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , in the temperature range of -150 to 300  $^{\circ}\text{C}$ . Constant operating parameters were kept for all the samples in order to obtain comparable data.

### 2.4. Hydrolysis of nitrile groups from starch-g-PAN

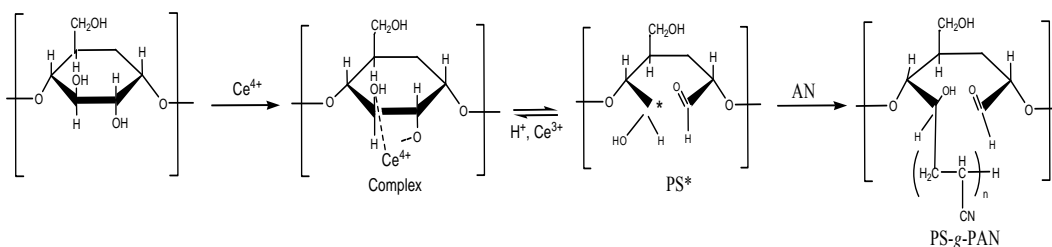
Hydrolysis reaction of the nitrile groups from starch-g-PAN (sample GPS2a) was performed varying the hydrolysis time, i.e. 10, 4 and 2 h, as follows: 1 g of grafted copolymer and 15 mL of NaOH 2.5 M were heated at 88  $^{\circ}\text{C}$ . After hydrolysis, a homogeneous solution has been obtained. To completely remove the hydrolysis agent, purification by dialysis of the hydrolyzed sample was performed until a neutral pH (about 72 h). The water soluble polymer was recovered by freeze-drying.

The content in carboxylate groups of the copolymer has been determined by polyelectrolyte titration using a particle charge detector PCD 03, Müteck GmbH, Germany (Mütek PCD-Titrator). The particle charge detector includes a Teflon piston, which moves up and down in a cylindrical Teflon cell containing the polyelectrolyte solution in the slit between the cylinder and piston. Displacement of the ions cloud around the polymer chains stuck to the porous wall of Teflon cylinder creates the streaming potential at the gold electrode pair located in upper and bottom parts of the cell. The concentration of the charged groups after hydrolysis was evaluated by titration with a standard solution of a strong oppositely charged polyelectrolyte, poly(diallyldimethylammonium chloride) (PDADMAC), with a concentration of  $10^{-3}$  mol/L. The concentration of the negatively charged groups in the examined solution was calculated from the amount of standard solution needed to reach the zero value of the streaming potential. The measurements were made in triplicate at room temperature.

## 3. Results and discussion

### 3.1. Synthesis of starch-g-PAN with $\text{Ce}^{4+}$ as free-radical initiator

The mechanism of graft copolymerization of AN on starch in the presence of  $\text{Ce}^{4+}$  as free radical initiator is expected to take place according to Scheme 1. The complex formed between  $\text{Ce}^{4+}$  and the -OH groups of PS at the C-2 and C-3 positions decomposes to generate the free radicals,  $\text{Ce}^{4+}$  ions being reduced to  $\text{Ce}^{3+}$  with the release of a proton. The grafting of AN has occurred at the active sites of PS.



*Scheme 1. Mechanism of grafting AN on PS with  $\text{Ce}^{4+}$  as free radical initiator.*

The nitrogen content of the two fractions separated from the samples prepared in different conditions is presented in Table 2.

Table 2. Nitrogen content of fraction *a*, monomer conversion and percentage of grafting.

Sample code	Nitrogen content of fraction <i>a</i> , %	Nitrogen content of fraction <i>b</i> , %	Conversion of monomer, %	PG, %	PG <sup>a</sup> , %
GPS1	18.13	0.68	59.16	59.4	218.38
GPS2	12.0	2.05	53.78	54	83.59
GPS3	13.1	2.08	22.35	44.7	99.3
GPS4	3.4	1.48	4.94	6	15.1
GPS5	2.8	1.58	5.55	4.6	11.8

<sup>a</sup> Percentage of grafting in fraction *a*;

As Table 2 shows, the nitrogen content of the fractions *a* is in the range 2.8 – 18.13 wt.%, as a function of the grafting conditions. In the fractions *b*, the nitrogen content was low compared with the nitrogen content of the fractions *a*. When the reaction was initiated with CAN the nitrogen content obtained was lower than in the case of reaction initiated with Ce(SO<sub>4</sub>)<sub>2</sub>. Furthermore, the elemental analysis (content in C and H) of the fractions *b* was very close to that theoretical of the anhydroglucose unit (AGU) (results not shown here). Thus, the elemental analysis gave the first indication that the grafting process did not take place on the whole sample of starch, but more probable only on one of the two major constituents. Another difference between the fractions *a* on the one hand, and *b* on the other hand, was the solubility of the fraction *a* only in DMSO and DMF, and of the fractions *b* in both DMSO and water.

Based on the nitrogen content of fraction *a*, the monomer conversion (*C*), and the percentage of grafting (PG) have been calculated with equations 1 and 2, respectively, their values being included in Table 2.

$$C = \frac{\text{weight of PAN}}{\text{weight of AN}} \times 100 \quad (1)$$

$$PG = \frac{\text{weight of PAN}}{\text{weight of starch}} \times 100 \quad (2)$$

As Table 2 shows, in the case of Ce(SO<sub>4</sub>)<sub>2</sub> utilization, the monomer conversion and the percentage of grafting decreased when the molar ratio between AN and AGU decreased [27]. For CAN as initiator, the percentage of grafting dramatically decreased when the ratio between AN and AGU decreased from 1.885 (synthesis GPS3) to 0.945 (synthesis GPS5).

FT-IR spectroscopy brought clear information about the structural changes after grafting of PAN on PS. FT-IR spectra of fractions *a* and *b* separated from the synthesis GPS2 (Table 2) are presented in Figure 1.

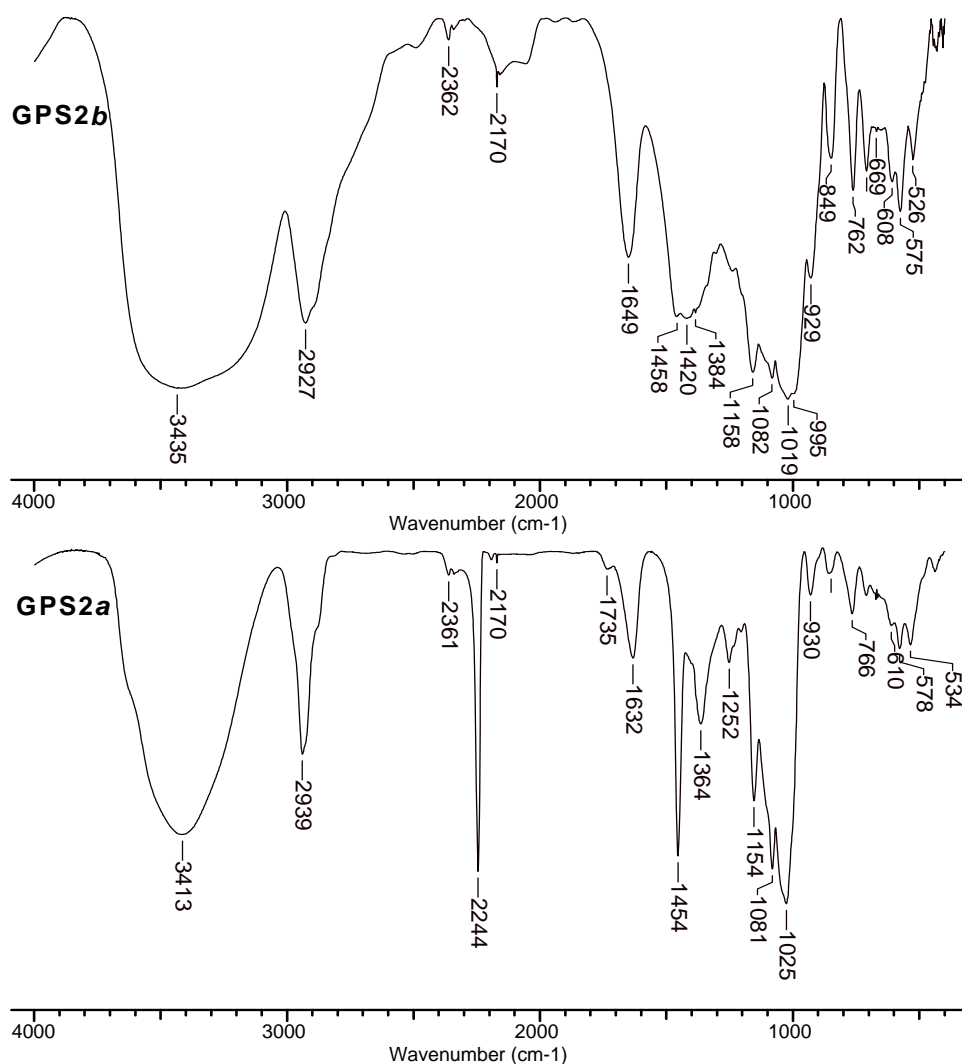


Fig. 1. FT-IR spectra of GPS2a and GPS2b

According to the literature, the FT-IR spectrum of PS contains the following characteristic peaks: a broad band between 3600 and 3200  $\text{cm}^{-1}$ , due to the stretching vibrations of O–H groups, a peak at 2927  $\text{cm}^{-1}$  (C–H aliphatic stretching), a peak at 1650  $\text{cm}^{-1}$ , which could be a feature of –OH bending, due to water absorbed in amorphous regions of starch, 1160, 1081, and 1015  $\text{cm}^{-1}$ , attributed to stretching of C–O bond from the AGU ring [8,26,28]. The FT-IR spectrum of PAN contains the following characteristic peaks: 2941  $\text{cm}^{-1}$ , assigned to C–H stretching, a peak at 2244  $\text{cm}^{-1}$ , assigned to –CN stretching, and at 1455  $\text{cm}^{-1}$ , for C–H bending. The peak at 1631  $\text{cm}^{-1}$ , can be assigned to –OH bending, due to absorbed water [29].

The FT-IR spectrum of the fraction GPS2a contains the characteristic peaks of both starch and PAN as follows: the peak at 2939  $\text{cm}^{-1}$ , assigned to C–H stretching, the high content of PAN grafted on PS is supported by the intense band at 2244  $\text{cm}^{-1}$ , corresponding to the –CN stretching, the band at 1632  $\text{cm}^{-1}$ , assigned to –OH bending, the characteristic peaks of the AGU ring can be seen at 1154, 1081, 1025 and 930  $\text{cm}^{-1}$ . The FT-IR spectrum of fraction GPS2b contains only the characteristic bands of starch, and no band which would support the presence of PAN. Moreover, the position of the characteristic bands suggests that the amylopectin would be the main component of this fraction [30]. Thus, FT-IR spectra support the selective grafting of PAN on PS, in the synthesis conditions used in this study.

$^1\text{H-NMR}$  spectroscopy brought definite information about the structures of the fractions separated after the grafting process compared with those of PAN and PS. The  $^1\text{H-NMR}$  spectra of the synthesis GPS2 fractions *a* and *b* are presented in Figure 2.

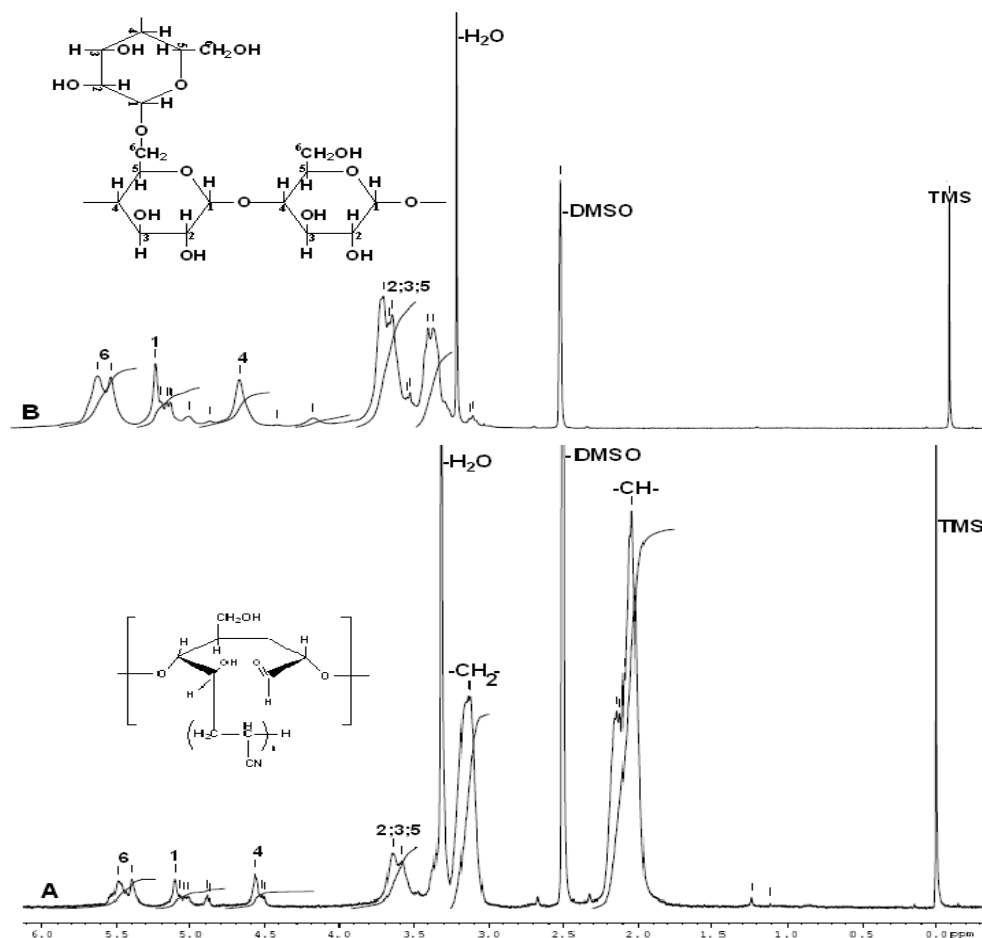


Fig. 2. The  $^1\text{H}$  NMR spectra of GPS2a (A) and GPS2b (B)

The characteristic peaks of PAN are located at 2.0 ppm, assigned to protons from  $-\text{CH}_2$  groups, and at 3.1 ppm, assigned to protons from  $-\text{CH}$  groups [29]. In the  $^1\text{H}$ -NMR spectrum of PS, the characteristic peaks were located at: 3.65 ppm, attributed to the hydrogen linked to the  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_5$  carbons, at 4.58 ppm, attributed to the protons linked to the  $\text{C}_4$  carbon, at 5.1 ppm, attributed to the hydrogen linked to the  $\text{C}_1$  carbon, and at 5.5 ppm, assigned to the hydrogen linked to the  $\text{C}_6$  carbon [29]. The  $^1\text{H}$ -NMR spectrum of the fraction GPS2a (Figure 2, spectrum A) contains the characteristic peaks of both starch and PAN, confirming the grafting of PAN onto starch. The characteristic peaks of the PAN were found at 2.0 ppm, attributed to  $\text{CH}_2$ -, and at 3.1 ppm, assigned to  $\text{CH}$ -bonds. The peaks characteristic of PS were found at 3.65 ppm, 4.58 ppm, 5.1 ppm, and at 5.5 ppm.

The  $^1\text{H}$ -NMR spectrum of the fraction GPS2b (spectrum B) contains only the characteristic peaks of starch, found at 5.5 ppm, attributed to the hydrogen linked to the  $\text{C}_6$ , at 5.1 ppm, assigned to the hydrogen linked to the  $\text{C}_1$ , at 4.6 ppm, assigned to the hydrogen linked to the  $\text{C}_4$ , at 3.65 ppm, assigned to the hydrogen linked to the  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_5$ . According to the literature [30,31], spectrum B is characteristic for amylopectin.

The selectivity in grafting PAN on PS found in this study could be ascribed to the differences in the reactivity of amylose and amylopectin, taking into account the high content of amylopectin branches in the crystalline domains and the location of amylose mainly in amorphous domains [10,11].

Further evidence for the grafting selectivity has been given by DSC thermograms presented in Figure 3.

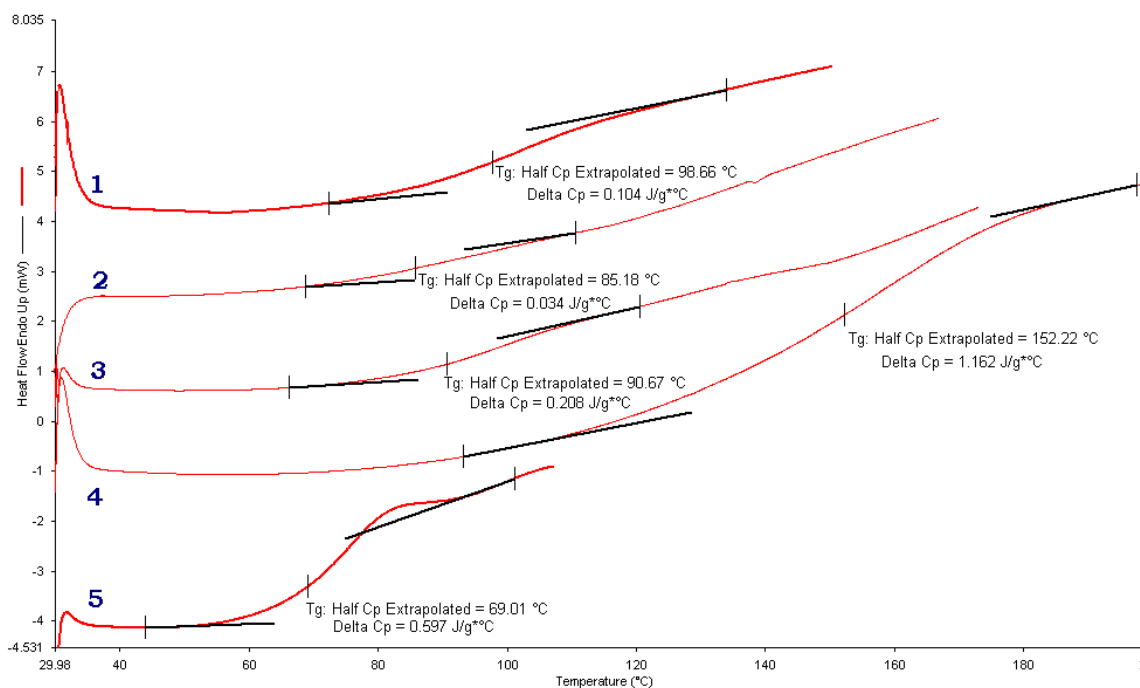


Fig. 3. DSC thermograms of: (1) PAN; (2) PS; (3) GPS2a; (4) GPS2a.h; (5) GPS2b

The  $T_g$  values of PAN and PS, found in literature, are around 100 °C and 70 °C, respectively [32,33]. As Figure 3 shows, the values of  $T_g$  found in our study for PAN and PS are as follows: 98.66 °C and 85.18 °C, respectively. The  $T_g$  value found for GPS2a of 90.67 °C is located between the  $T_g$  values of PAN and PS, and this supports the structure of this fraction as PS-*g*-PAN and not a mixture of PAN homopolymer with one constituent of starch. The  $T_g$  value of 69 °C, found for the fraction *b* isolated from the synthesis GPS2 (Table 2), indicates a pure constituent of PS, which remained non-grafted in the reaction conditions used in this work, this being the most probable amylopectin.

### 3.2. Hydrolysis of the starch-*g*-PAN

The nitrogen content of fraction GPS2a varying the time of hydrolysis is presented in Table 3.

Table 3. Nitrogen content of fraction a after hydrolysis

Sample code	Time of hydrolysis, h	Nitrogen content, %
GPS2a.h1	2	4.37
GPS2a.h2	4	3.61
GPS2a.h3	10	2.45

The nitrogen content decreased with the time of the hydrolysis down to 2.45%. The low content in nitrogen would suggest the presence of some residual nitrile groups or the amide groups generated as an intermediary stage in the formation of COO<sup>-</sup> groups.

First information on the structure of the GPS2a.h3 has been given by the FT-IR spectra. FT-IR spectra of the fraction GPS2a before and after hydrolysis are presented in Figure 4.

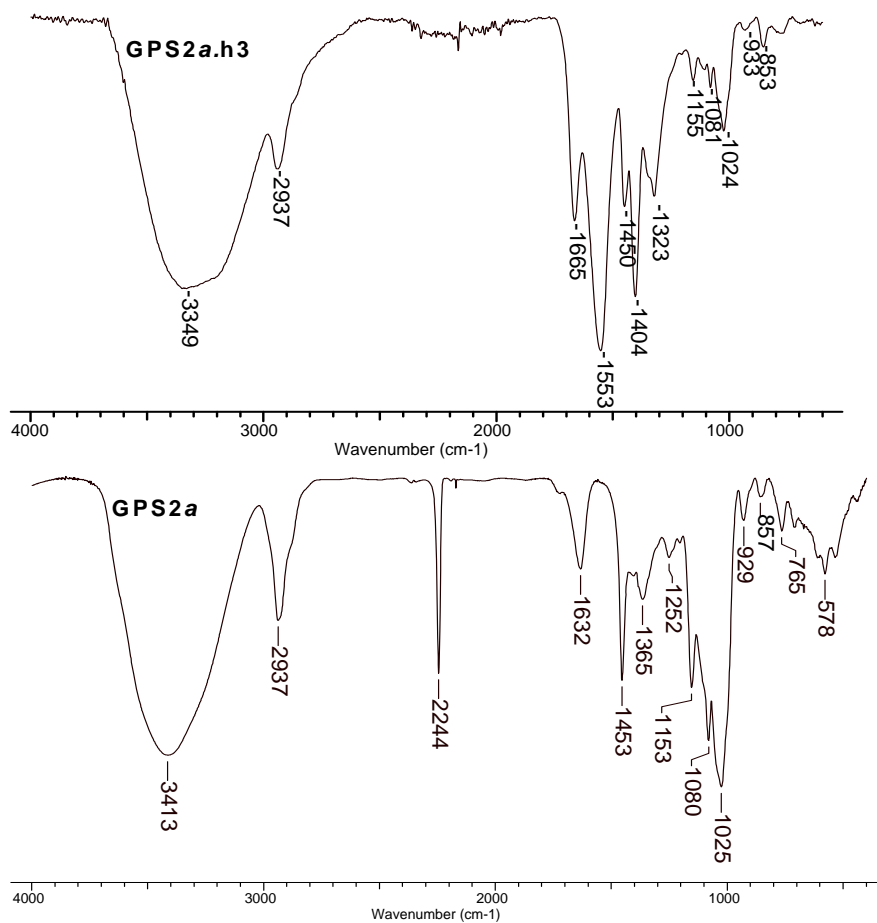


Fig. 4. FT-IR spectra of GPS2a and GPS2a.h3.

The FT-IR spectrum of GPS2a.h3 shows the absence of the band at  $2241\text{ cm}^{-1}$ , characteristic to the nitrile groups, and some new bands assigned to the functional groups generated by the base hydrolysis, such as amide and carboxylate, as follows:  $1665\text{ cm}^{-1}$  assigned to the stretching vibrations of the C=O bond in amide group (amide I band);  $1553\text{ cm}^{-1}$  assigned to the deformation vibrations of the  $-\text{COO}^-$  groups;  $1450\text{ cm}^{-1}$  assigned to C-H bending;  $1404\text{ cm}^{-1}$  assigned to  $-\text{COO}^-$  groups. The bands at  $1155\text{ cm}^{-1}$ ,  $1081\text{ cm}^{-1}$ , and  $1024\text{ cm}^{-1}$ , characteristic to the AGU rings in the polysaccharide backbone are still visible after the hydrolysis.

The  $^1\text{H-NMR}$  spectra of GPS2a before and after hydrolysis are presented in Figure 5.



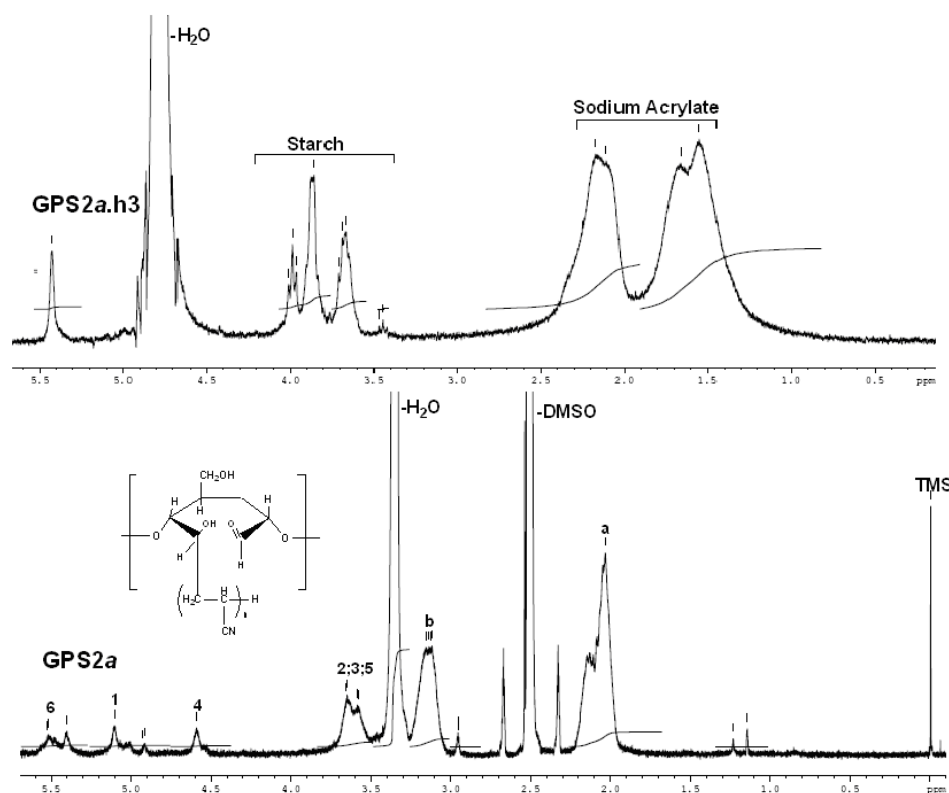


Fig. 5.  $^1\text{H-NMR}$  spectra of GPS2a and GPS2a.h

As can be observed, the  $^1\text{H-NMR}$  spectrum of GPS2a.h contains some peaks between 3.5 ppm and 4.0 ppm assigned to the protons of the AGU of PS, and also two peaks at 1.4 ppm and 2.3 ppm, which can be assigned to the protons of the sodium acrylate.

After the hydrolysis, all acidic groups are in form of sodium salt. Therefore, the content in poly(sodium acrylate) grafted on starch has been quantitatively determined by polyelectrolyte titration with PDADMAC as oppositely charged polyelectrolyte. Thus, the content of PANa in GPS2a.h was found to be 0.695 g PANa/g.

#### 4. Conclusion

The paper deals with the grafting of PAN on PS by the free radical grafting of acrylonitrile with  $\text{Ce}^{4+}$  ions. A selective grafting of AN mainly on amylose and less on amylopectin has been demonstrated in this work by elemental analysis, FT-IR and  $^1\text{H-NMR}$  spectroscopy, and DSC. The monomer conversion and grafting percentage in the reaction initiated with  $\text{Ce}(\text{SO}_4)_2$  was three times higher than in the case of reaction initiated with CAN. By the hydrolysis of PAN grafted on PS, a water soluble polyanion has been obtained, the nitrogen content decreasing with the time of hydrolysis from 4.37 to 2.45 %. The FT-IR analysis of the water soluble polymers suggests mainly the presence of amide groups, which constitute the intermediary stage in the alkaline hydrolysis of the nitrile groups to  $\text{COO}^-$ .

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