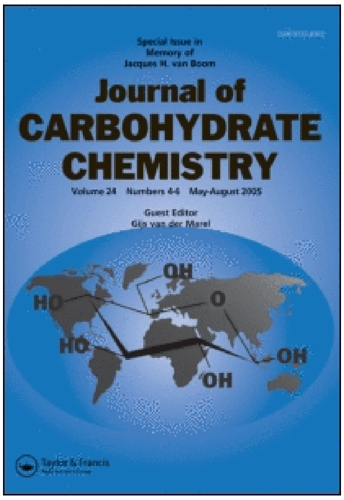


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Synthesis, NMR Study and Preliminary Sorption Properties of two *N*-Benzyl Sulfonated Chitosan Derivatives

Grégorio Crini[a]; Giangiacomo Torri[b]; Bernard Martel[a]; Marek Weltrowski[c]; Michel Morcellet[a]; Cesare Cosentino[b]
[a] Laboratory of Macromolecular Chemistry, URA CNRS 351, University of Lille, Villeneuve, France [b] G. Ronzoni Institute for Chemical and Biochemical Research, Milan, Italy [c] Textile Technology Centre, Quebec, Canada

To cite this Article Crini, Grégorio , Torri, Giangiacomo , Martel, Bernard , Weltrowski, Marek , Morcellet, Michel and Cosentino, Cesare(1997) 'Synthesis, NMR Study and Preliminary Sorption Properties of two *N*-Benzyl Sulfonated Chitosan Derivatives', Journal of Carbohydrate Chemistry, 16: 4, 681 — 689

To link to this Article: DOI: 10.1080/07328309708007346

URL: http://dx.doi.org/10.1080/07328309708007346

J. CARBOHYDRATE CHEMISTRY, 16(4&5), 681-689 (1997)

SYNTHESIS, NMR STUDY AND PRELIMINARY SORPTION PROPERTIES OF TWO *N*-BENZYL SULFONATED CHITOSAN DERIVATIVES[1]

Grégorio Crini,[a*] Giangiacomo Torri,[b] Bernard Martel,[a] Marek Weltrowski,[c] Michel Morcellet[a] and Cesare Cosentino[b]

[a] Laboratory of Macromolecular Chemistry, URA CNRS 351, University of Lille, 59655 Villeneuve d'Ascq, France
[b] G. Ronzoni Institute for Chemical and Biochemical Research, G. Colombo, 81, Milan 20133 Italy
[c]Textile Technology Centre, 3000 rue Boullé, J2S 1H9 Saint Hyacinthe, Quebec, Canada

Received July 22, 1996 - Final Form April 11, 1997

ABSTRACT

Two chitosan based sorbents for the uptake of metallic cations in acidic solutions were synthesized. Chitosan was reacted with 2-formylbenzene sodium sulfonate and 4-formyl-1,3-benzene sodium disulfonate in the presence of $NaCNBH_3$ to yield *N*-benzyl mono and disulfonate derivatives of chitosan. NMR spectra confirmed the presence of benzyl sulfonate groups which were subsequently used to determine the degree of substitution. The results of sorption experiments for mono and divalent metals at pH=2 are reported.

INTRODUCTION

Heavy metal ions are pollutants species which are preferably removed from industrial effluents. The sorption of heavy metals using biopolymers is one of the reported methods for the removal of such metals even in low concentrations (ppm or ppb levels). The efficiency and the selectivity of this method are attributed to chelation and ion exchange mechanisms. Commercial chitosan, a polymer consisting of β(1-4) linked 2-deoxy-2-amino-D-glucopyranose with some 2-deoxy-2-acetamido-D-glucopyranose (ca 20%), is obtained by deacetylation of chitin, a natural polymer extracted from crustacea shells. Chitosan and some of its derivatives have been reported to be efficient transition metal sorbents.[2-6] However, chelating amino polymers such as chitosan[7] or synthetic poly(vinylamine) based resins[8-10] have a low efficiency in metal uptake in the low pH range present in acidic waste waters because of protonation of the amino groups. Moreover, amino polymers such as chitosan are soluble in acidic media and therefore cannot be used as sorbents under these conditions[11] excepted after crosslinking.

Muzzarelli[12] reported a sulfuric acid ammonium sulfate pre-treated chitosan with a good capacity for some transition metal ions uptake in solution at pH=3. In the case of carboxymethyl[13] and carboxybutyl[14] derivatives of chitosan, both amino and carboxylic groups are involved in the metal chelation. However, their activity is depressed by lowering the pH. We have previously reported[15] the synthesis and the sorption capacities of two *N*-benzyl sulfonic derivatives of chitosan with improved cation exchange properties in acidic pH.

The method consists of the preparation of *N*-aryl derivatives by reductive alkylation,[16] a technique discovered by Borch *et al*,[17] and applied to chitosan by Hall and Yalpani.[18] The sorption capacity of our sulphonated chitosan derivatives were tested on the following heavy metal ions : Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+}. The sorption capacities of the disulfonated compound was higher than those of the monosulfonated compound. This phenomenon was attributed to the amphoteric character of the monosulfonated derivative.

In this paper, we report the synthesis and sorption characteristics for these two new chitosan derivatives with a number of metallic cations. The results of an NMR study on the chitosan derivatives allowed us to confirm their structure and to explain the reason why one of the synthesized compounds is not effective in the sorption experiments.

RESULTS AND DISCUSSION

The synthesis of the target *N*-benzyl sulfonated derivatives **A1** and **B1** is outlined in the Scheme. Characterization of **A1** and **B1** was carried out by NMR spectroscopy. The ^1H and ^{13}C NMR spectra for compounds **A1** and **B1** are shown in Figures 1 and 2, respectively. An important contribution to the characterization was achieved by using a pure-absorption heteronuclear multiple bond correlation (HMBC) experiment.[19] Substitution was demonstrated by the correlations between the CH_2 protons of the sulfonate group with the C2 of glucosamine and aromatic carbons.

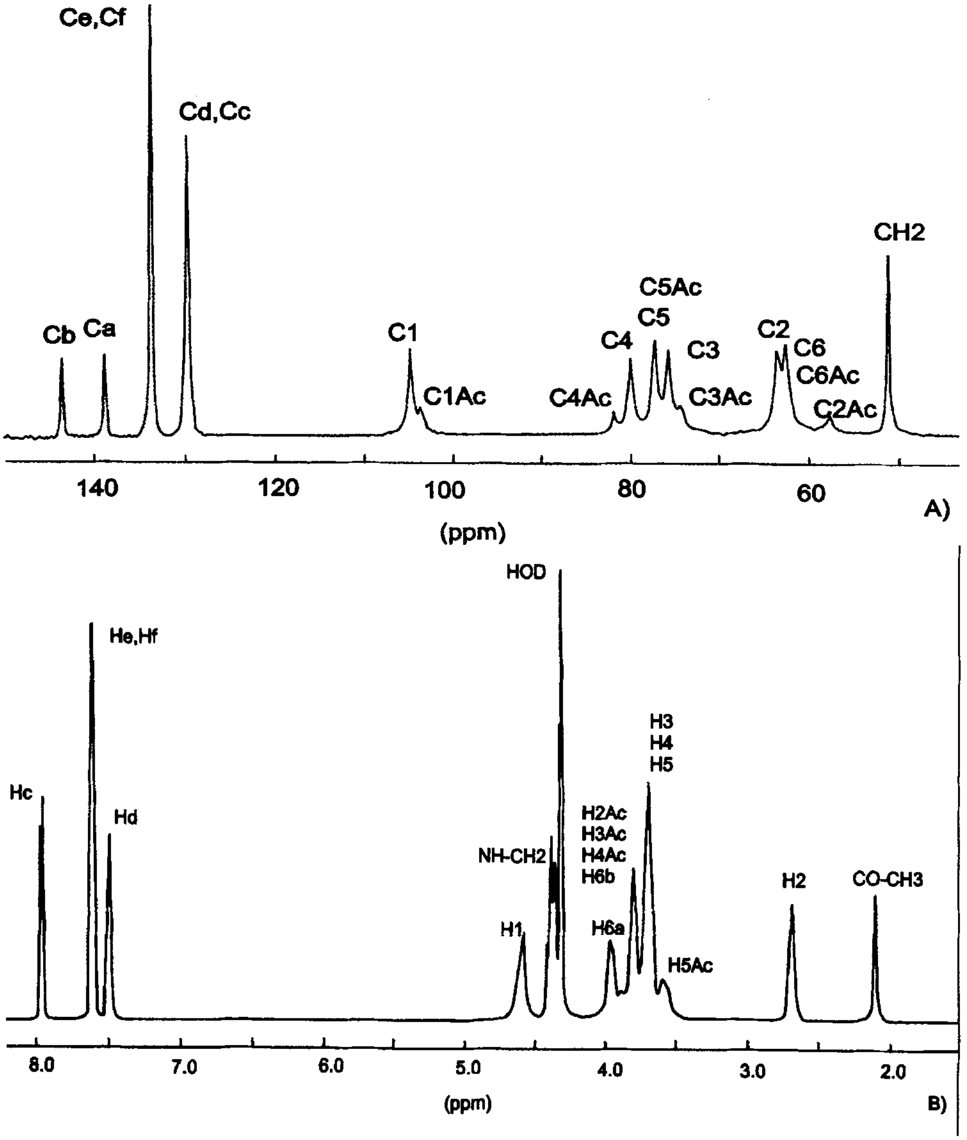


Figure 1. (A) ^{13}C and (B) ^{1}H NMR spectra of chitosan **A1**.

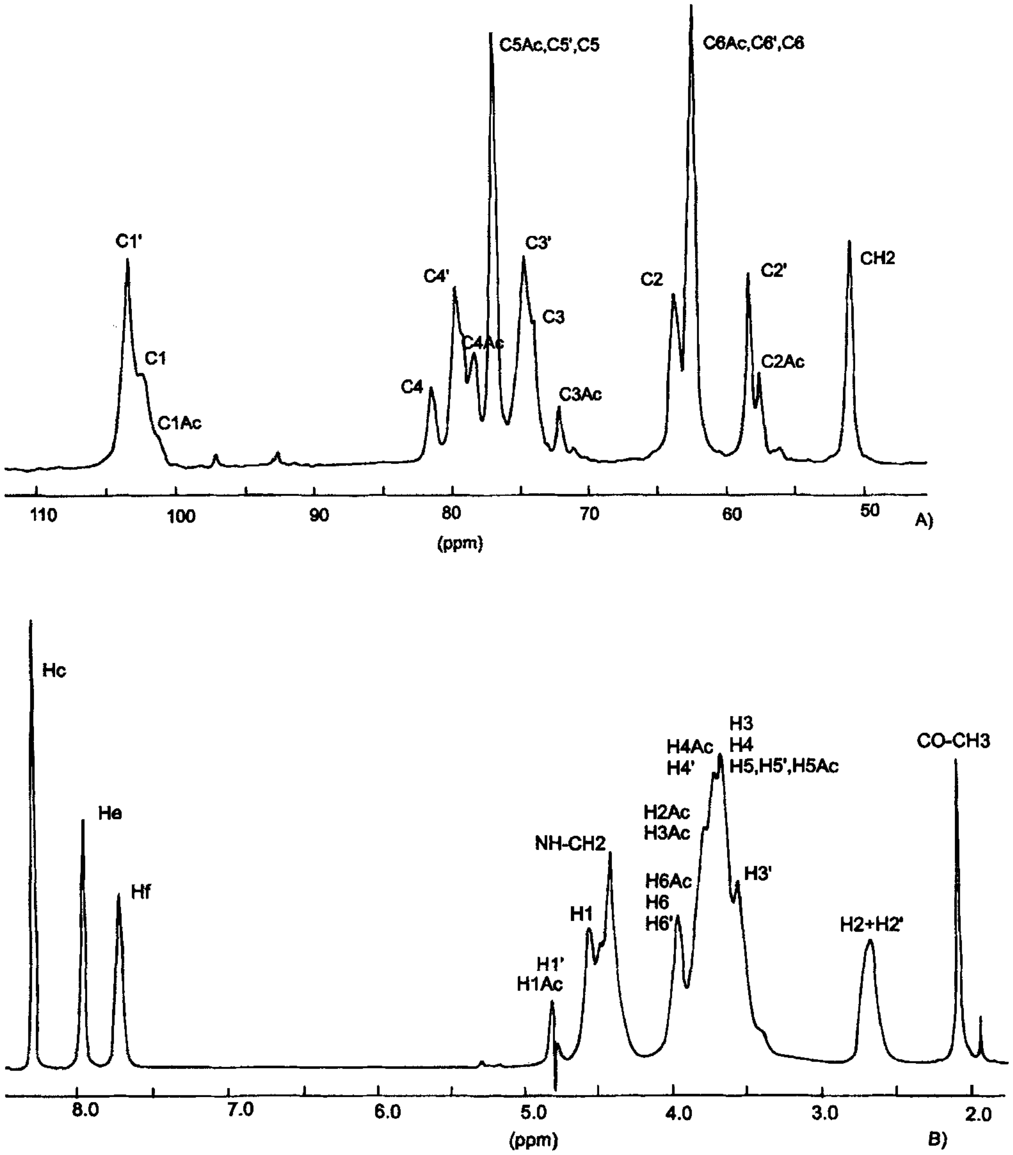


Figure 2. (A) ^{13}C and (B) ^{1}H NMR spectra of chitosan **B1**.

Table : Weight percentage of metal uptake by the sorbents **A1** and **B1** at pH=2 [a,b]

Sorbent	(a) Cd^{2+}	(a) Zn^{2+}	(b) Ni^{2+}	(c) Pb^{2+}	(c) Cu^{2+}	(c) Fe^{3+}	(c) Cr^{3+}
A1	0	0	0	0	-	0	7
B1	-	-	3	4	3	19	23

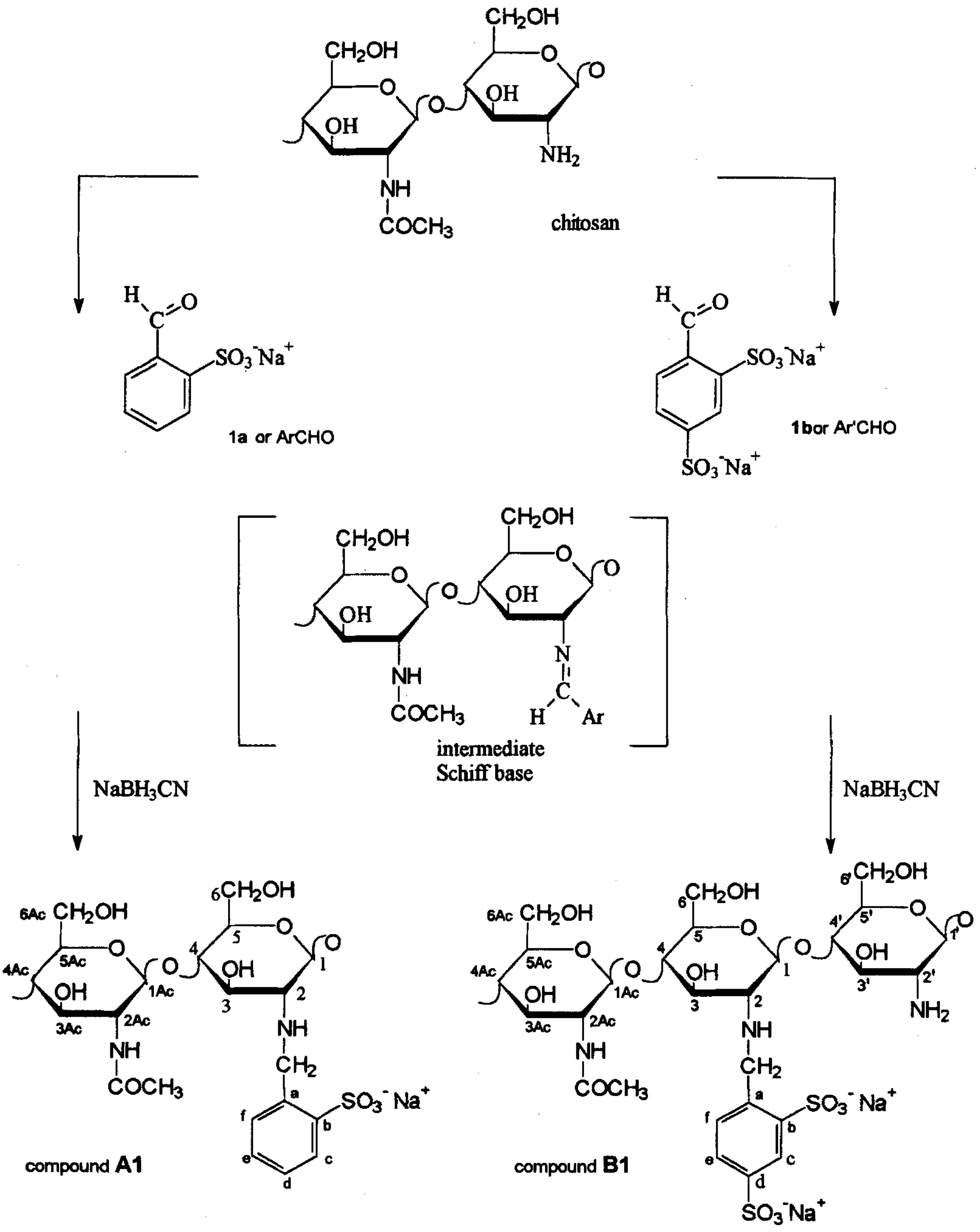
a, **A1** contains 83% units bearing benzyl sulphonate groups and 17% *N*-acetyled groups. **B1** contains 47% units bearing benzyl disulphonate groups, 17% *N*-acetyled groups and 36% unsubstituted amine groups. b, 100 mg of sorbent in 50 mL of solution. Initial concentration : (a) 1 ppm; (b) 2.5 ppm; (c) 5 ppm.

A comparison of the two ^{13}C NMR spectra shown in Figures 1B and 2B corresponding to the structure of compounds **A1** and **B1** (Scheme) respectively, demonstrates the increased degree of complexity in compound **B1**. For **B1**, three patterns of substitution prevail : *N*-acetylated, *N*-benzyl sulfonate and free amine. There are two different C2 signals at 59.1 and 64.2 ppm corresponding to unsubstituted (free amino) and *N*-benzyl sulphonate substituted glucosamine units. In compound **A1**, there is no detectable glucosamine with free amino at C2 and the *N*-benzyl sulphonate substituted C2 signal appears at 64 ppm.

Using ^{1}H NMR data, we have found the overall degree of substitution is 83% and 47% (compared with 80% and 50% by elemental analysis) for the mono- and the disulfonated derivatives respectively. The table reports the results obtained for the uptake of divalent and trivalent metallic ions by the modified chitosans using a batch method. No uptake was recorded with the divalent cations Cd^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} when **A1** was used as sorbent.

In the case of the trivalent cations, only Cr^{3+} was slightly adsorbed by the monosulfonated derivative. Some decrease in the concentration of Ni^{2+}, Pb^{2+}, Cu^{2+} is detectable for **B1** but remains rather low for **A1**. Sorption is more evident for Fe^{3+} and Cr^{3+} solutions whose concentrations decrease from 5 ppm to 4.05 and 3.84 ppm respectively. This observation confirms the importance of the cation charge and the ionic mechanism of the sorption.

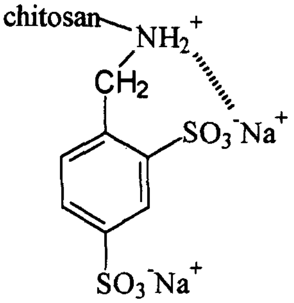
The difference in the uptake of the metallic cations between the mono and the disulfonated sorbents cannot be explained solely by the fact that the former contains a greater amount of sulfonate equivalent per gram of polymer. Compound **B1** has 1.25 times more sulfonate groups than **A1** but its uptake for Cr^{3+} is about 3 times greater. This phenomenon can be explained by the global charge of the polymer. At pH=2, the primary and secondary amino groups of both chitosan derivatives are undoubtedly protonated. This induces repulsive interactions with the positively charged ions. Furthermore, another attractive electrostatic interaction may occur between the positive ammonium sites and the


chitosan
1a or ArCHO
1b or Ar'CHO
intermediate Schiff base
NaBH3CN
NaBH3CN
compound A1
compound B1

Scheme

sulfonate groups (see below). As a consequence, the negatively charged character of sulfonate groups is reduced and the adsorption properties of the derivatives are weakened.

Such an interaction has already been reported by Naggi *et al.*[18] who showed the possible occurence of an intramolecular zwitterionic interaction in chitosan 6-sulfate that increased the rigidity of the chain segments at low pH values. The higher sorption values obtained for disulfonated derivatives can be attributed to the second sulfonate group in the *para* position which has good accessibility for the metallic cations in solution and cannot intramolecularly interact with the positively charged amino groups. Therefore, the global charge of the polymer, under these experimental conditions, is neutral for the monosulfonated derivative but negative for the disulfonated derivative.



CONCLUSION

In this paper the syntheses of two new derivatives of chitosan have been described. An NMR study was used to characterize these polymers, assign all proton and carbon signals and confirm their structures. Comparison of the sorption capacities of both chitosan derivatives led us to conclude that the SO_3^- group in the ortho position is hardly invoved in the binding with the metallic species.

The originality of both compounds is their inversed pH domain of solubility compared to the parent polymer. This characteristic allowed us to study their sorption capacity in aqueous acidic media without further crosslinking reaction. The practical use of such sorbents may be rather limited for the treatment of waste waters because of their apparent low performances, especially for **A1**. Despite this fact, the same chemical modifications have been attempted onto chitosan based filters and gave much more better results in metal sorption experiments.[21]

EXPERIMENTAL

Materials. Chitosan was supplied by Protan and contained 20% of *N*-acetyl groups in glucosamine as determined by ^1H NMR. Sodium cyanoborohydride, 2-

formylbenzenesulfonic acid, sodium salt dihydrate (**1a**, see Scheme), 4-formyl-1,3-benzenedisulfonic acid, disodium salt hydrate (**1b**, see Scheme) were obtained from Aldrich chemicals (Strasbourg, France).

Monosulfonate chitosan derivative A1 (see Scheme). Chitosan (5g) was dissolved in 500 mL of a 0.5% aqueous solution of acetic acid. Methanol (450 mL) was added to the chitosan solution. Sodium cyanoborohydride (10g) was dissolved in the solution under vigorous stirring and after 3 min aldehyde **1a**, dissolved in 150 mL of methanol, was added. In the next 3 min, the viscosity of the solution decreased and a white precipitate appeared. Stirring was continued for 4 h at ambient temperature. The mixture was then filtered and the precipitate was washed successively with 3 L of distilled water and 1 L of acetone. The product was dried overnight at 40 °C to give a light brown powder after crushing.

Disulfonate chitosan derivative B1 (see Scheme). The method for the disulfonate derivative **B1** was similar to that applied to the monosulfonate derivative **A1** except that aldehyde **1b** was dissolved in 150 mL of distilled water. The amount of methanol in the initial solution was 650 mL. The modified polymer was washed with water and acetone by the centrifugation method.

Metal sorption experiments. The sorption capacities of the products were evaluated by the batch method. Typically, 100 mg of polymer were added to 50 mL of solution containing 5 ppm of the metal ion. The solution was prepared from a standard 1000 ppm solution diluted with a 0.05 M HCl-KCl buffer (pH=2). The solution was then stirred on a rotating shaker. Preliminary kinetic experiments showed that 90 min contact time was sufficient for equilibrium to be reached. The sorbent was then removed by centrifugation and the concentration of metal ions in the solution was measured by atomic absorption spectrometry (Perkin Elmer 1100 B AAS Spectrometer). The results (Table) are reported in terms of weight percentage of uptake of the metal.

NMR spectroscopy. The ^{13}C NMR spectra were obtained at 75.47 MHz on a Bruker AC 300 spectrometer (Bruker, Karlsruhe, Germany) equipped with a 10 mm probe. The ^{1}H NMR spectra were measured at 500 MHz on a Bruker AMX 500 spectrometer equipped with a 5 mm $^{1}H/X$ inverse probe and a Bruker BGU gradient unit z system. The spectra were obtained with presaturation of the HOD signal. Chitosan sulfonate derivatives were dissolved in 0.1 M NaOD solutions. All measurements were performed at 338 K. The chemical shift values were referenced to external sodium 3-(trimethylsilyl)propionate-d4 (TSP from E. Merck, Darmstadt, Germany). Quantification of the degree of substitution of the glucosamine units was performed by integration of the area of the ^{1}H signals at 2.65 ppm (compound **A1**) and at 2.69 ppm (compound **B1**) (see Figures 1 and 2).

REFERENCES

1. Presented at the *XVIIIth International Carbohydrate Symposium*, Milan, Italy, July 21-26, 1996.
2. J.M. Randall, V.G. Randall, M. Mc Donald, R.N. Young and M.S. Masri, *J. Appl. Polym. Sci.*, **23**, 727 (1979).
3. C. Peniche-Covas, L.W. Alvarez and W. Arguelles-Monal, *J. Appl. Polym. Sci.*, **46**, 1147 (1992).
4. I.N. Jha, L. Iyengar and A.V.S. Prabhakara Rao, *J. Environ. Eng.*, **114**, 962 (1988).
5. J.R. Deans and B.G. Dixon, *Water Research*, **26**, 469 (1992).
6. C.J. Brine, P.A. Sandford and J.P. Zikakis (Eds.), in *Advances in Chitin and Chitosan*, Elsevier Applied Science London (1991).
7. R.A.A. Muzzarelli, in *Chitin*, Pergamon Press, p 140 (1977).
8. H. Tbal, J. Morcellet, M. Delporte and M. Morcellet, *J. Macromol. Sci., Pure Appl. Chem.*, **29**, 699 (1992).
9. H. Tbal, D. Le Maguer, J. Morcellet, M. Delporte and M. Morcellet, *Reactive Polym.*, **17**, 207 (1992).
10. L. Janus, J. Morcellet, M. Delporte and M. Morcellet, *Eur. Polym. J.*, **10**, 1185 (1992).
11. R.A.A. Muzzarelli, in *Chitin*, Pergamon Press, p 278 (1977).
12. R.A.A. Muzzarelli, in *Chitin*, Pergamon Press, p 144 (1977).
13. L. Dobetti and F. Delben, *Carbohydr. Polym.*, **18**, 273 (1991).
14. F. Delben, S. Stefanich and R.A.A. Muzzarelli, *Carbohydr. Polym.*, **19**, 17 (1992).
15. M. Weltrowski, B. Martel and M. Morcellet, *J. Appl. Polym. Sci.*, **59**, 647 (1996).
16. G.A.F. Roberts, in *Chitin Chemistry*, Macmillan, p 175 (1992).
17. R.F. Borch, M.D. Bernstein and H.D. Durst, *J. Am. Chem. Soc.*, **93**, 1153 (1971).
18. L. Hall and M. Yalpani, *J. Chem. Soc., Chem. Commun.*, 1153 (1980).
19. G. Crini, M. Guerrini, G.Torri, M. Morcellet, M. Weltrowski and B. Martel, *Carbohydr. Polym.*, in press.
20. A.M. Naggi, G. Torri, T. Compagnoni and B. Casu, in *Chitin in Nature and Technology*, R.A.A. Muzzarelli, C. Jeuniaux, G. Gooday, Eds., Plenum Press, New York, p 379 (1985).
21. B. Martel, M. Weltrowski and M. Morcellet, in *Advances in Chitin Science*, A. Domard, J. Jeuniaux, R.A.A. Muzzarelli, G. Roberts, Eds., J. André (Lyon, France), p 291 (1996).