

Synthetic Tannins Structure by MALDI-TOF Mass Spectroscopy

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ABSTRACT: The structure, polymeric nature, and oligomers distribution of six types of commercial synthetic tannins (syntans) were determined by MALDI-TOF mass spectrometry. The syntans examined were: (i) polycondensation oligomers of sulfonated phenol and 4,4'-dioxydiphenylsulfone with formaldehyde and sodium bisulfite; (ii) sodium salts of polycondensation oligomers of phenol and sulfonated phenol with formaldehyde and urea; (iii) sodium salts of polycondensation oligomers of sulfonated phenol with formaldehyde and urea; (iv) sodium and ammonium

salts of polycondensation oligomers of sulfonated naphthalene with formaldehyde; and (v) a sulfonated phenolic novolak resin. The oligomers distribution indicated that the relative abundance of oligomers from trimer to higher degrees of polymerization varied from 70% to more than 90% according to the different syntans tested. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1339–1347, 2009

Key words: syntans; MALDI; resins; tannins; polycondensation; structure

INTRODUCTION

Vegetable tannins have been used to tan leather either alone or accompanying other tanning agents for several thousand years. Forestry derived vegetable tannins have however a considerable disadvantage, namely, they present marked darkening problems when exposed to light and even worse they give leather that does shrink already at relatively lower temperatures than chrome tanning.^{1,2} Conversely, synthetic tanning agents (syntans) give either lighter colored leathers and high resistance to degradation induced by light.

Synthetic tanning agents (syntans), namely, sulfonated phenol-formaldehyde resins, sulfonated melamine-formaldehyde resin,^{1,2} and sulfonated naphthalene-formaldehyde resins are today prepared and used industrially in great amounts for tanning hides into leather presenting special properties or having a particularly light color or improved light stability.^{1,2} Although their general structure is known from the materials and the preparation procedures used, their exact oligomeric structures and in particular their structure distribution have not been investigated before. This article deals with the investigation of commercial syntans oligomer struc-

tures and structure distribution by MALDI-TOF mass spectrometry.

Since its introduction by Karas and Hillenkamp in 1987,³ matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has greatly expanded the use of mass spectrometry toward large molecules and has revealed itself to be a powerful method for the characterization of both synthetic and natural polymers.^{4–16} Fragmentation of analyte molecules on laser irradiation can be substantially reduced by embedding them in a light absorbing matrix. As a result, intact analyte molecules are desorbed and ionized along with the matrix and can be analyzed in a mass spectrometer. This soft ionization technique is mostly combined with time-of-flight (TOF) mass analyzers. This is so as TOF-MS present the advantage of being capable to provide a complete mass spectrum per event, for its virtually unlimited mass range, for the small amount of analyte necessary and the relatively low cost of the equipment.

EXPERIMENTAL

Tannin types

Six types of commercial synthetic tannins (syntans) were used for MALDI-TOF analysis, all supplied from Silva Chimica, S.Michele Mondovi', Italy, namely (i) Blancotan BC, polycondensation oligomers of sulfonated phenol and 4,4'-dioxydiphenylsulfone with formaldehyde and sodiumbisulfite; (ii) sodium Blancotan HLF, sodium salts of polycondensation

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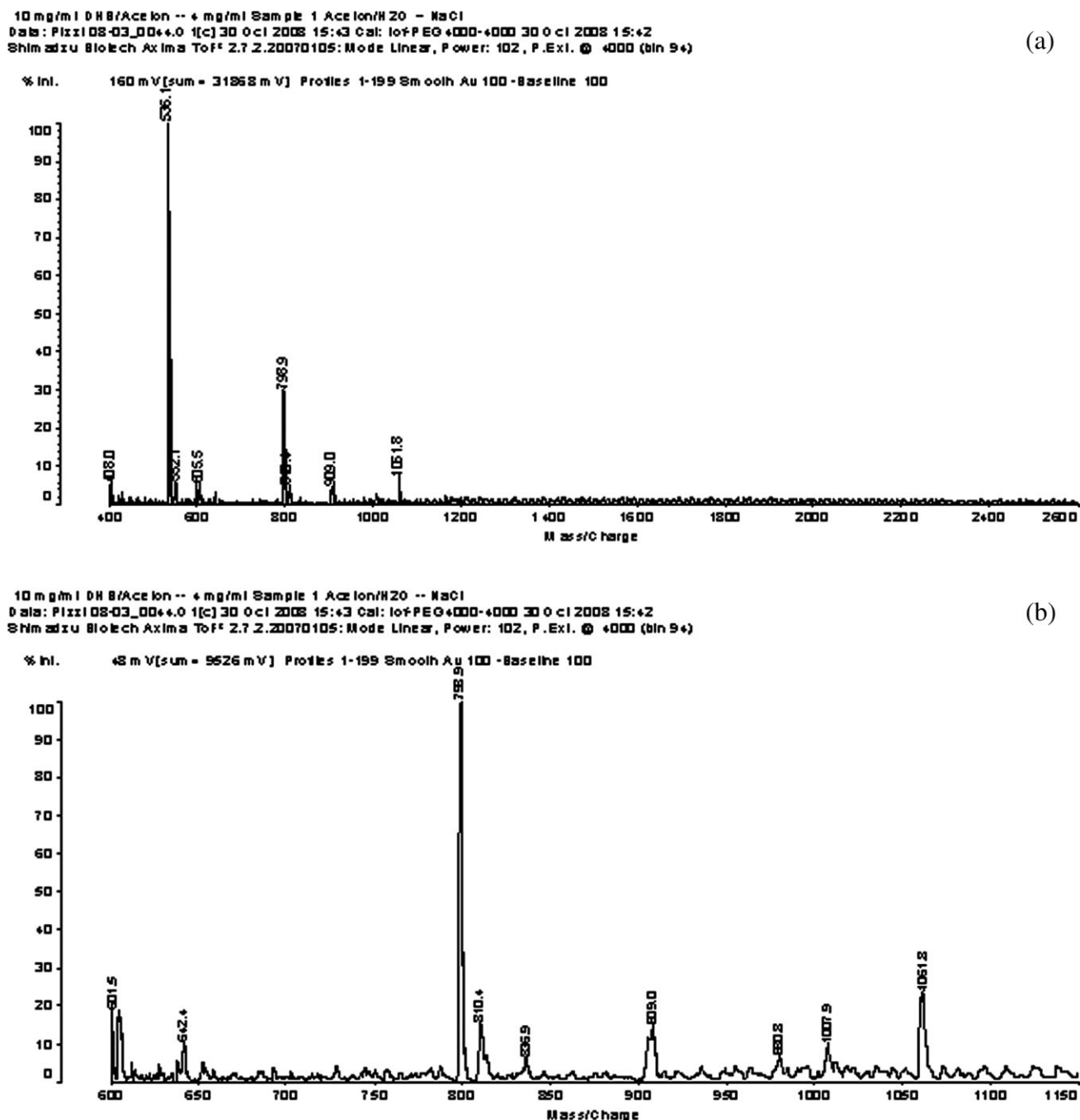


Figure 1 Positive ion mode MALDI-TOF mass spectrum of polycondensation oligomers of the reaction of sulfonated phenol and 4,4'-dioxydiphenylsulfone with formaldehyde and sodium bisulfite. (a) 400–2600 Da. (b) Details of the 600–1150 Da.

oligomers of sulfonated phenol and phenol with formaldehyde and urea; (iii) sodium Blancotan HLF/PC, sodium salts of polycondensation oligomers of sulfonated phenol with formaldehyde and urea; (iv) sodium Blancotan SN, sodium salts of polycondensation oligomers of sulfonated naphthalene with formaldehyde; (v) ammonium Blancotan SN, ammonium salts of polycondensation oligomers of sulfonated naphthalene with formaldehyde; and (vi) Blancotan PRV, sulfonated phenolic novolak resin.

MALDI-TOF-MS

The spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 kV acceleration voltage), 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns.

MALDI-TOF sample preparation

Positive mode

The polymer samples were dissolved in acetone (4 mg/mL, 50/50% vol). The sample solutions were mixed with a acetone solution (10 mg/mL in acetone) of the matrix. 2,5-dihydroxy benzoic acid was used as the matrix. For the enhancement of ion formation, NaCl was added to the matrix (10 mg/mL in water). The solutions of the sample and the matrix were mixed in the proportions 3 parts matrix solution + 3 parts polymer solution + 1 part NaCl solution and 0.5 to 1 μ L of the resulting solution mix were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. The dry droplet sample preparation method was used.

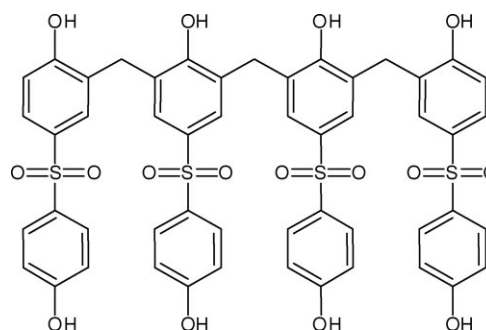
Negative mode

The polymer samples were dissolved in acetone/water (4 mg/mL, 50/50% vol). The sample solutions were mixed with a tetrahydrofuran (THF) solution (10 mg/mL in acetone) of the matrix. Harmin was used as the matrix. The solutions of the sample and the matrix were mixed in equal proportions, and the resulting solution mixes were placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into the spectrometer. The dry droplet sample preparation method was used.

RESULTS AND DISCUSSION

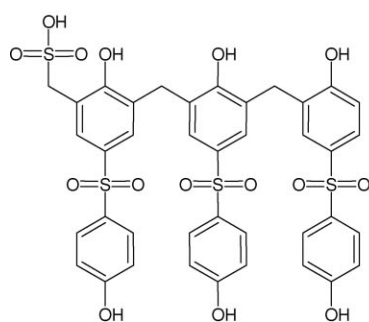
The oligomer types and oligomers distribution for the Blancotan BC syntan are derived from the positive ions MALDI-TOF spectra in Figure 1(a,b) and the negative ions spectra in Figure 2(a,b). In the positive ions spectra the main series of peaks is the 536 Da, 798 Da, and 1062 Da corresponding after subtracting 23 Da for the Na⁺ matrix additive to the oligomers of molecular weight 512, 774, and 1037. These are respectively the dimer, trimer, and

tetramer of the polycondensation reaction of 4,4'-dioxydiphenylsulfone with formaldehyde. Thus, the structure of the 1037 Da tetramer is

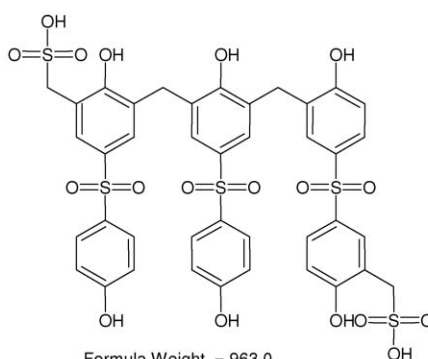


Formula Weight = 1037.1

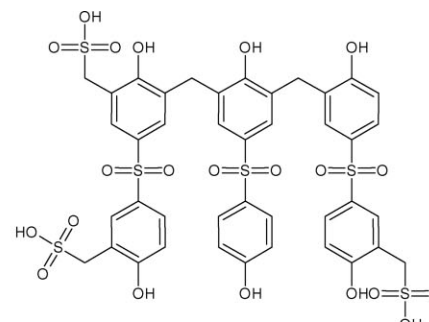
Also visible is a small peak at 606 Da (a cluster at 601, 606, and 610 Da) that is instead the most abundant peak in the negative ions mode in Figure 2(a,b). In Figure 2(a,b) instead, the negative ions mode in which the peaks indicate directly the molecular mass of the oligomer without need to subtract 23 Da for the Na⁺, it is noticeable the series of peaks at 344 Da, 512 Da, 606 (601–610) Da, 700 Da, 794 Da, 869 Da, 963 Da, 1057 Da, 1131 Da, 1225 Da, and 1319 Da. These are a series of 4,4'-dioxydiphenylsulfone polycondensates with formaldehyde some presenting on their structure one, two, or three methylene sulfonic acid groups linked to the structure of the oligomer. The only oligomer that does not present a methylene sulfonic acid group is the one at 512 Da, the structure of which is identical to that of the dimer observed in Figure 1(a) at 536 Da. Thus, the series above corresponds to respectively methylenesulfonated monomer, dimer, monomethylenesulfonated dimer, dimethylenesulfonated dimer, trimethylenesulfonated dimer, monomethylenesulfonated trimer, diomethylenesulfonated trimer, trimethylenesulfonated trimer, monomethylenesulfonated tetramer, dimethylenesulfonated tetramer, and trimethylenesulfonated tetramer. An example of the formulas of the three trimers being:



Formula Weight = 868.9



Formula Weight = 963.0



Formula Weight = 1057.1

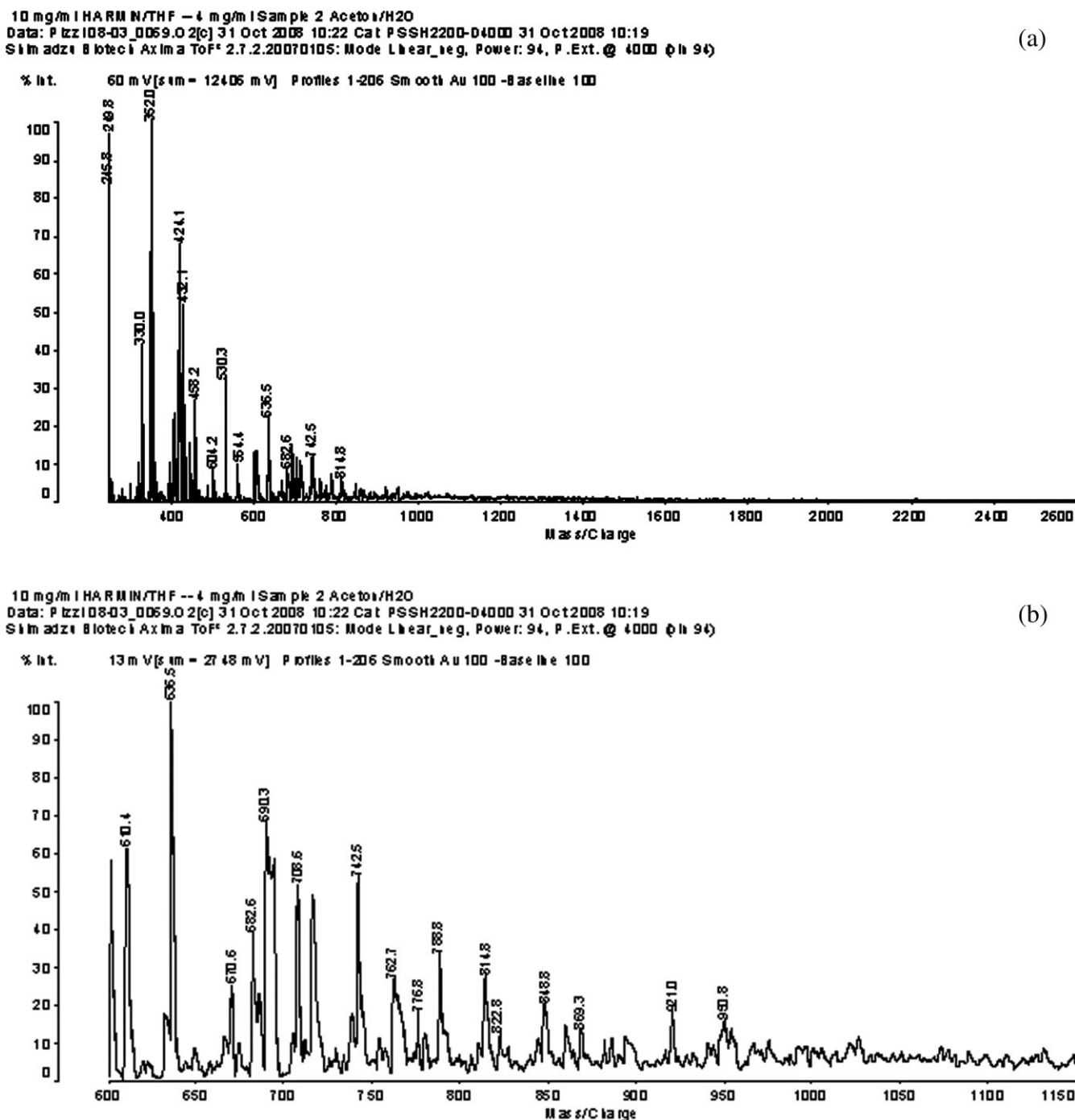
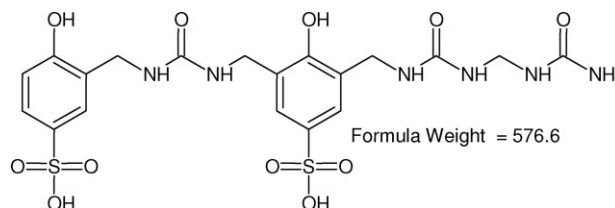


Figure 2 Negative ion mode MALDI-TOF mass spectrum of polycondensation oligomers of the reaction of sulfonated phenol and 4,4'-dioxydiphenylsulfone with formaldehyde and sodium bisulfite. (a) 400–2600 Da. (b) Details of the 600–1150 Da.

Even more interesting are the results of the polycondensates of sodium Blancotan HLF PC, a syntan formed by the cocondensation of sulfonated phenol, urea, and formaldehyde. These are cocondensation products with formaldehyde of sulfonated phenol and urea. In the positive ions mode in Figure 3, the main peak at 601 Da corresponds to a cocondensation pentamer of three ureas and two sulfonated phenols having structure



The peak at 483–485 Da corresponds to $\text{Ph}-\text{CH}_2-\text{U}-\text{CH}_2-\text{Ph}-\text{CH}_2\text{OH}$. The rest of the peaks

10 mg/ml DHB/Acetic ion -- 4 mg/ml Sample 3 Acetic/H2O - NaCl
 Data: F111 08-03_0050.M3[C] 300 Cl 2008 15:57 Cal: IofPEQ+000+000 300 Cl 2008 15:42
 S/Nm adzu Bloch Axima ToF 2.7.2.0070 105: Mode Linear, Power: 113, P.Exl. @ +000 (bin 94)

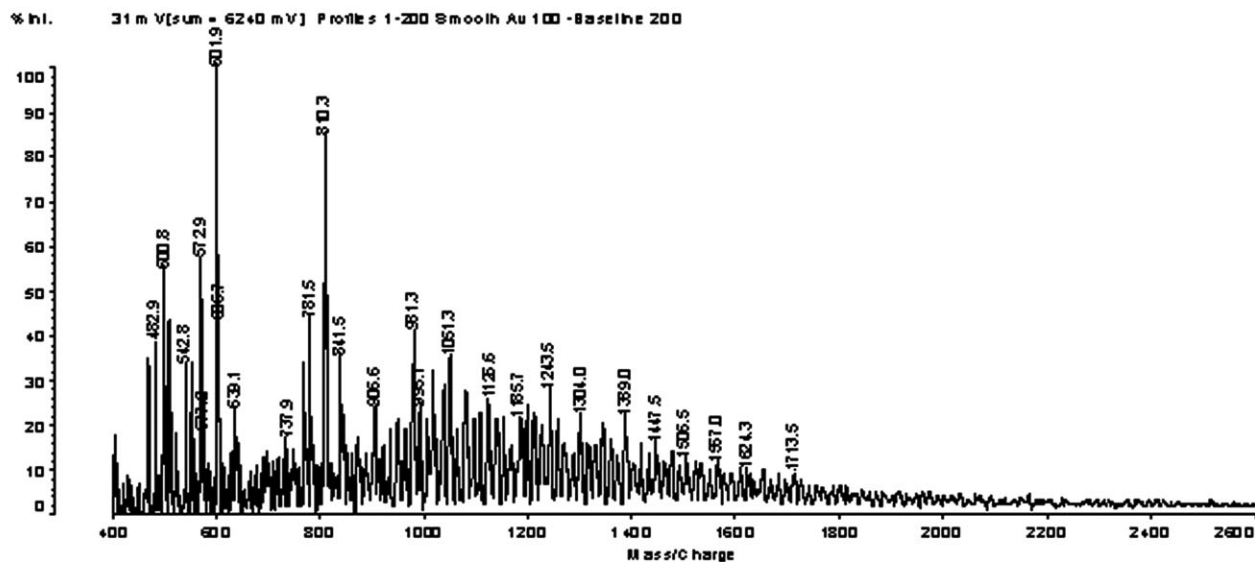


Figure 3 Positive ion mode MALDI-TOF mass spectrum of sodium salts of polycondensation oligomers from the reaction of phenol and sulfonated phenol with formaldehyde and urea.

TABLE I
Sodium Blancotan HLF and HLF/PC Oligomers

Peak Da	Method positive or negative ions	Relative proportion (%)	Oligomer type
246	Neg.	11	HO ₃ S-Ph-CH ₂ -NHCONH ₂
330	Neg.	7	(HO ₃ S) ₂ -Ph-CH ₂ -NHCONH ₂
(352)	Neg.	HLF)	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph
(403)	Pos.	HLF)	⁻ O ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph-CH ₂ OH
408	Neg.	9	(HO ₃ S) ₂ -Ph-CH ₂ -NHCONH-SO ₃ H
422	Neg.	22	(HO ₃ S) ₂ -Ph-CH ₂ -NHCON(-CH ₂ ⁺)-SO ₃ H or HO ₃ S-Ph-CH ₂ -[NHCONH-CH ₂] ₂ -Ph
432	Neg.	18	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph-SO ₃ H
(458)	Neg.	HLF)	HO ₃ S-Ph-CH ₂ -NHCONH-[CH ₂ -Ph] ₂
(475)	Pos.	HLF)	⁻ O ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph-CH ₂ -NHCONH-CH ₂ OH
483	Pos.		HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph(-SO ₃ H)-CH ₂ OH
504	Neg.	14	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph(-SO ₃ H)-CH ₂ -NHCONH ₂ , or HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -NHCONH-CH ₂ -Ph-SO ₃ H
(508)	Pos.	HLF)	⁻ O ₃ S-Ph-CH ₂ -NHCONH-[CH ₂ -Ph] ₂
(530)	Neg.	HLF)	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph-CH ₂ -NHCONH-CH ₂ -Ph
(581)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₂ -[CH ₂ -Ph] ₂ -CH ₂ OH
601	Pos.		HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph(-SO ₃ H)-[CH ₂ -NHCONH-] ₂ -H
(636)	Neg.	HLF)	HO ₃ S-Ph-[CH ₂ -NHCONH] ₂ -[CH ₂ -Ph] ₃
(687)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₂ -[CH ₂ -Ph] ₃ -CH ₂ OH
690	Neg.	8	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph(-SO ₃ H)-CH ₂ -NHCONH-CH ₂ -Ph-SO ₃ H, or all type H-NHCONH-CH ₂ -NHCONH-CH ₂ -[Ph(-SO ₃ H)] ₃
(759)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₃ -CH ₂ OH
(742)	Neg.	HLF)	HO ₃ S-Ph-[CH ₂ -NHCONH] ₂ -[CH ₂ -Ph] ₄
763	Neg.	8	HO ₃ S-Ph-CH ₂ -NHCONH-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[NHCONH-CH ₂] ₂ -Ph-SO ₃ H or all combinations type H[-NHCONH-CH ₂] ₂ -NHCONH-CH ₂ -[Ph(-SO ₃ H)] ₃
(814)	Neg.	HLF)	HO ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₄
(865)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₄ -CH ₂ OH
942	Neg.	1.8	all combinations type H-[-NHCONH-CH ₂] ₃ -NHCONH-CH ₂ -Ph-CH ₂ -[Ph(-SO ₃ H)] ₃
(971)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₅ -CH ₂ OH
1023	Neg.	1.2	all combinations type H-[-NHCONH-CH ₂] ₃ -NHCONH-CH ₂ -[Ph(-SO ₃ H)] ₄
(1077)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₆ -CH ₂ OH
(1183)	Pos.	HLF)	⁻ O ₃ S-Ph-[CH ₂ -NHCONH] ₃ -[CH ₂ -Ph] ₇ -CH ₂ OH

The oligomers belonging only to HLF and not to HLF/PC are indicated between parenthesis. U: urea residue; Ph: phenol residue.

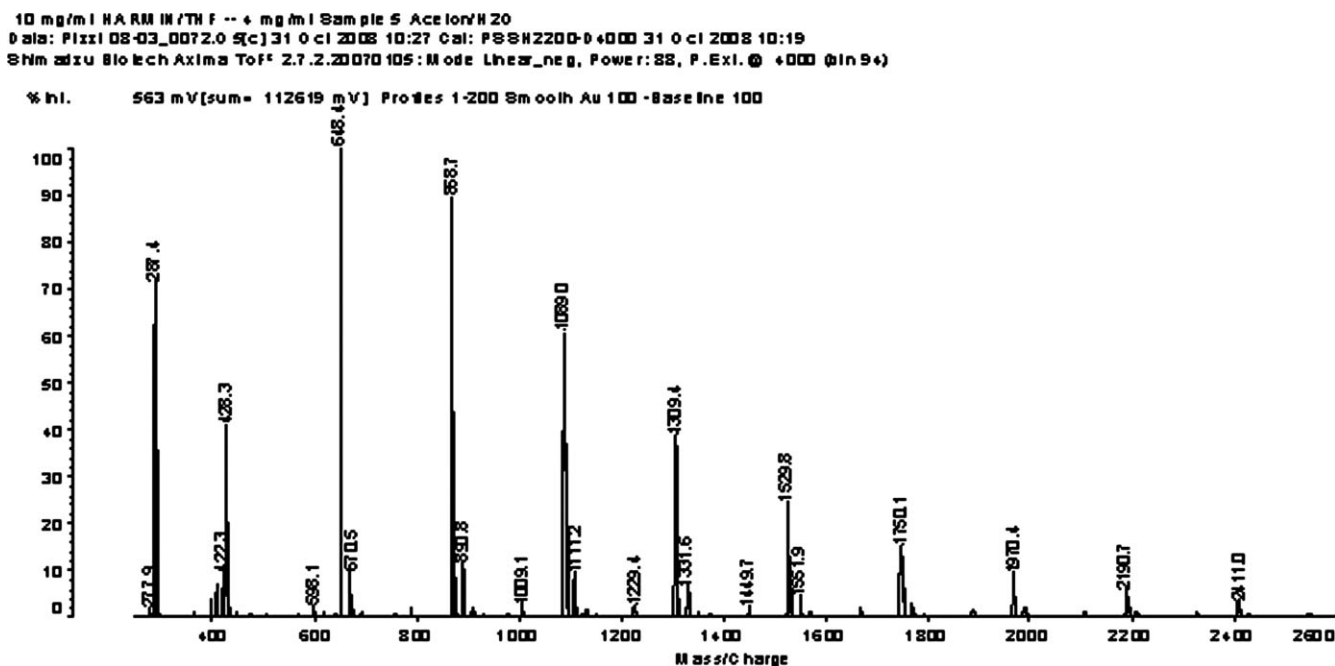


Figure 4 Negative ion mode MALDI-TOF mass spectrum of sodium/ammonium salts of polycondensation oligomers from the reaction of sulfonated naphthalene with formaldehyde.

are shown in Table I for both Blancotan HLF and Blancotan HLF PC. The series of phenol-urea-formaldehyde oligomers and of sulfonated phenol-urea-formaldehyde oligomers for these two syntans are shown in Table I. In general, a single sulfonic group per chain is present on these oligomers with the exception of the series of peaks at 690 Da ($3 \times -\text{SO}_3\text{H}$), 763 Da ($3 \times -\text{SO}_3\text{H}$), 942 Da ($3 \times -\text{SO}_3\text{H}$), and 1023 Da ($4 \times$

$-\text{SO}_3\text{H}$). As regards the oligomers dimension, oligomers up to seven phenolic rings and three urea residues linked together by methylene bridges are observed as well as oligomers up to four ureas with four phenols (1023 Da). The relative proportion of these oligomers as indicated in Table I shows that about 70% is constituted of trimers and higher oligomers of higher molecular mass, these being predominant in this tannin extract.

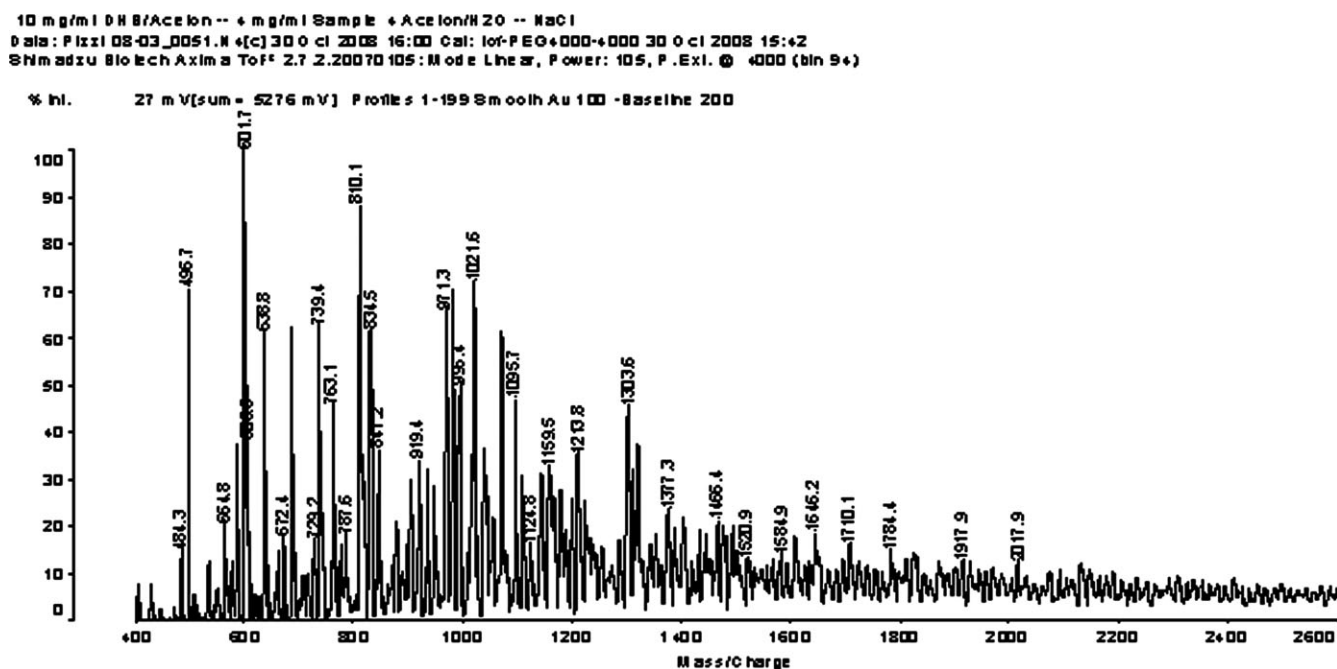


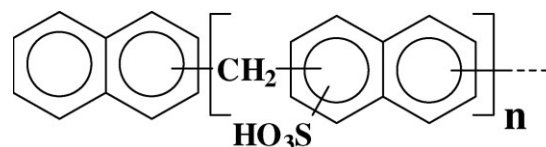
Figure 5 Positive ion mode MALDI-TOF mass spectrum of sodium/ammonium salts of polycondensation oligomers from the reaction of sulfonated naphthalene with formaldehyde.

TABLE II
Sodium and Ammonium Blancotan SN Oligomers

Peak Da	Method: positive or negative ions	Relative proportion (%)		Oligomer type
		Na	NH ₄	
428	Neg.	11.7	10.9	Naph-[CH ₂ -Naph(-SO ₃ H)-]
496	Pos.	-	-	HOCH ₂ -Naph-CH ₂ -Naph-CH ₂ ⁺
648	Neg.	30.9	26.0	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₂
689	Pos.	-	-	Naph-[CH ₂ -Naph] ₂ -CH ₂ ⁺
717	Pos.	-	-	HOCH ₂ -Naph-[CH ₂ -Naph] ₂ -CH ₂ ⁺
868	Neg.	27.2	23.4	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₃
1089	Neg.	16.1	13.5	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₄
1310	Neg.	7.7	10.4	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₅
1530	Neg.	3.7	6.8	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₆
1751	Neg.	2.1	3.9	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₇
1971	Neg.	0.6	2.6	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₈
2190	Neg.	-	1.5	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₉
2411	Neg.	-	1.0	Naph-[CH ₂ -Naph(-SO ₃ H)-] ₁₀

As regards, the syntans (sodium and ammonium Blancotan SN) these were prepared by the sulfonated product of the reaction of condensation of naphthalene with formaldehyde, the MALDI-TOF spectrum of which is shown in Figures 4 (negative ion mode) and 5 (positive ion mode). The series of peaks of the two compound are very similar and are both reported in Table II. The repeating motive in the spectra is of 220 Da. This is a monosulfonated naphthalene to which is linked a methylene bridge. The type of oligomers formed are shown in Table II. The main series of oligomers noted correspond to a succession of linear oligomers of up to 11 naphthalene units linked to each

other by methylene bridges, all repeating units being sulfonated, with the exception of the first one. The main series of oligomers can then be represented as having the following general structure



Where n is an integer number between 1 and 10 and where the sulfonic group is found both as

10 mg/ml HARM N/THF - 4 mg/ml Sample 20 Acetone/H2O
Data: P LZZ108-03_0073.06[c] 31 Oct 2008 10:29 Cat P SS H2200-04000 31 Oct 2008 10:32
Silmadz 8 kV Tech Axima ToF 2.7 2.20070 10S: Mode L bear_neg, Power: 88, P.Ext. @ 4000 phi 9 phi

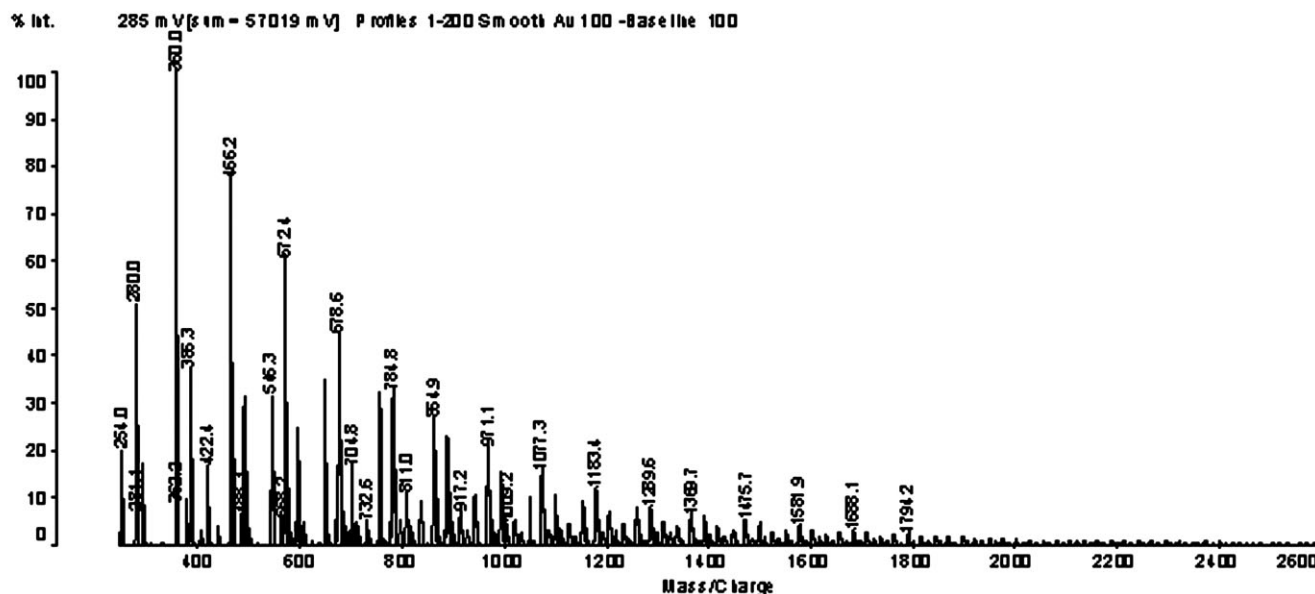


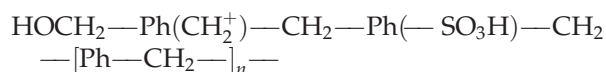
Figure 6 Negative ion mode MALDI-TOF mass spectrum of a sulfonated phenolic novolak resin syntan.

TABLE III
Sulfonated Phenol-Formaldehyde Novolak Oligomers of Syntan Blancotan PRV
Obtained by MALDI-TOF Negative Ion Mode

Peak Da	Method: negative ions. Relative proportion (%)	Oligomer type
254	3.4	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph-CH ₂ -
360	16.3	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph-CH ₂]- ₂ -
466	13.0	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph-CH ₂]- ₃ -
546	5.4	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₂ -
572	10.1	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₃ -
652	5.9	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₂ -
678	7.5	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₄ -
758	5.4	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₃ -
784	5.4	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₅ -
864	4.4	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₄ -
890	3.8	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₆ -
971	3.6	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₅ -
996	2.6	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₇ -
1077	2.9	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₆ -
1102	1.6	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₈ -
1183	2.3	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₇ -
1208	1.1	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -Ph(-SO ₃ H)-CH ₂ -[Ph-CH ₂]- ₉ -
1289	1.6	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₂ -[Ph-CH ₂]- ₈ -
1369	1.3	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₃ -[Ph-CH ₂]- ₈ -
1475	1.0	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₃ -[Ph-CH ₂]- ₁₀ -
1581	0.7	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₃ -[Ph-CH ₂]- ₁₁ -
1688	0.5	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₃ -[Ph-CH ₂]- ₁₂ -
1794	0.2	HOCH ₂ -Ph(CH ₂ ⁺)-CH ₂ -[Ph(-SO ₃ H)-CH ₂] ₃ -[Ph-CH ₂]- ₁₃ -

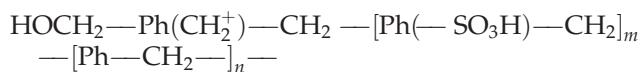
-SO₃H and as -SO₃⁻. In both cases in Table II, the relative proportion of oligomers from trimers upward is of just under 90% of the total.

The last syntan, a sulfonated phenol-formaldehyde novolak, (MALDI-TOF Spectrum in Fig. 6) present the oligomers shown in Table III. This is composed of two main parallel main series. The first of these presents general structure:



In which n = the sequence of integer numbers between 1 and 10, thus oligomers of up to 13 phenolic moieties. In this series of oligomers only one sulfonic group for each oligomer is present.

Parallel to this, there is the series of oligomers that are heavily sulfonated. Their general structure is



Where m is an integer number between 0 and 2, and n is an integer number between 1 and 9. Thus, for this series, oligomers of up to 12 phenolic rings are linked to each other by the methylene bridges

formed by reaction with formaldehyde. In Table III, the relative proportion of oligomers from trimers upward is of 96% of the total.

CONCLUSIONS

The structure of the six different syntans analyzed by MALDI-TOF indicated that the products obtained by commercial synthesis were composed of resin oligomers up to degrees of polymerization higher than what thought previously for these materials. The oligomers distribution indicated that the relative abundance of oligomers from trimer to higher degrees of polymerization varied from 70% to more than 90% according to the different syntans tested. Furthermore, these syntans are often composed of mixtures in which parallel series of sulfonated and nonsulfonated oligomers both occur.

References

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