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Synthesis and characterization of fully biobased aromatic polyols - Oxybutylation of condensed tannins towards new macromolecular architectures.

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Abstract

For the first time, different tannins were oxybutylated to obtain aromatic and fully biobased polyols. The main interest to use 1,2-butylene oxide (BO) instead of *e.g.*, propylene oxide is that BO can be easily biobased and biosynthesized from biomass. BO can be obtained by epoxidation of butane, produced from biobased butanol, synthesized by biotech. The oxybutylation was carry out using potassium hydroxide as a catalyst, in a high pressure batch reactor, without solvent, on agreement with the main principles of a green chemistry. Firstly, different biobased aromatic polyols have been synthesized from gambier tannin (*Uncaria gambir*) and have been fully characterized. To better understand the conditions and mechanisms of the synthesis, the influence of the tannin / BO ratio was assessed through the evolution of the hydroxyl content, homopolymer content, molar mass distributions and the corresponding viscosities. In addition, the thermal properties were evaluated to better understand the final molecular architectures. Secondly, selected conditions of synthesis were applied to other types of tannins from pine (*Pinus pinaster*), mimosa (*Acacia mearnsii*) and quebracho (*Schinopsis balansae* and *Schinopsis lorentzii)*. The corresponding results were

compared to extend this study. For all tannins, the number and length of grafted chains were carefully characterized. Great variations of reactivity have been shown between the different botanical sources. Taylor-made, fully biobased and controlled aromatic macropolyols can be obtained by modulating the main parameters of the oxybutylation reaction and the type of tannin botanical source.

Keywords

Tannin, oxybutylation, biobased, polyol, ^{31}P NMR, aromatic polymer

1. Introduction

Replacing fossil-based raw materials with renewable sources has recently shown a strong increasing trend.[1-3] Aromatic renewable source represents a high potential for the elaboration of new macromolecular structures. Studies based on aromatic renewable sources for the elaboration of biobased chemicals and polymers are therefore in the core of the current researches *e.g.*, the development of fully biobased PET. However aromatic structures are not so very common in the biomass. The main renewable biomass polymers based on aromatic units are lignins.[4] These latter are difficult to be clearly defined and fragmented to obtain efficient and reproducible building blocks or biopolymers, due to complex structures depending on the botanical source.[5] Tannins are after lignins the most abundant source of natural aromatic macromolecules, and they show a simpler polyphenolic structure. They are extracted from different plants and are classified into two main groups namely the hydrolysable and the condensed tannins. These latter are composed of complex condensation products of flavonoid units leading to bio-oligomers. The reactivity of tannins is essentially linked to their phenolic hydroxyl groups.[6-8] Depending on their botanical source, tannins structures may differ

considerably with regards to hydroxyl (OH) group content and molar mass, thus affecting different properties, such as the solubility.

The OH groups brought by the tannins have been considered for chemical modification *e.g.*, for polymer synthesis. They can be used in applications such as adhesives for wood,[6] epoxy resins [7] or foams.[9] Unfortunately, tannins show a limited reactivity due to different factors like a steric hindrance or a limited accessibility of the phenolic OH groups. Various strategies can be used to increase this reactivity,[6, 10] such as alkoxylation reactions.

Oxypropylation of biomass is a well-known method to increase the reactivity and the accessibility of the original OH groups brought by the bioproducts.[11] The oxypropylation was highly investigated on many different biomasses bearing OH groups such as lignins.[12-16] Very recently, this reaction has been used to modify tannins.[17] The resulting liquid polyols can be used as macropolyols (building blocks) to elaborate different macromolecular architectures.[13, 18] However, propylene oxide (PO), used in these reactions, is obtained from fossil sources and then, the final products are only partially biobased (less than 50%).

Other alkoxides could be employed such as the 1,2-butylene oxide (BO) which presents the great potential of being obtained from biosourced molecules after reaction of dehydration and epoxidation.[19, 20] Recently, biobased butanol was industrialized by industrial fermentation or white biotech.[21, 22] For instance, acetone–butanol–ethanol has been developed at an industrial level by fermentation from starch.[23] Another great advantage of BO is its lower toxicity compared to PO.[24, 25]

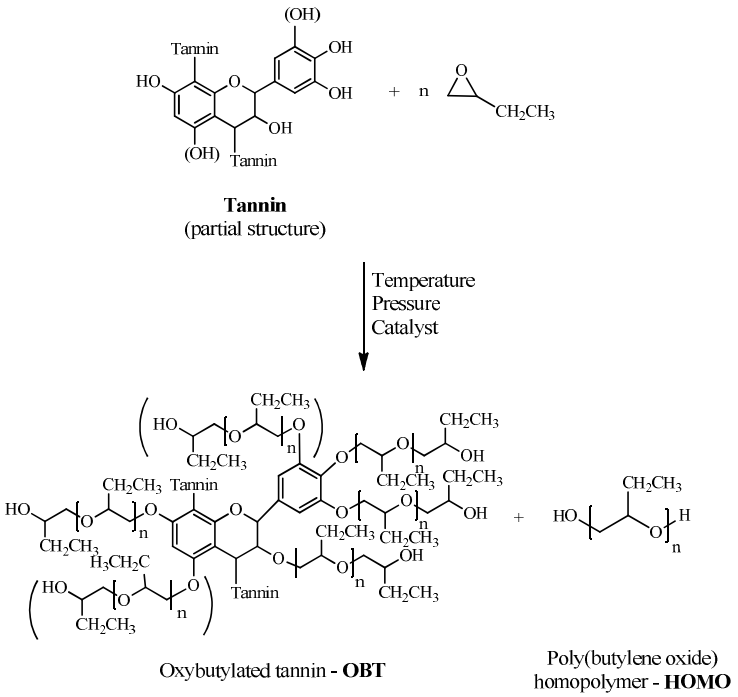


Fig. 1. Reaction scheme for tannin oxybutylation.

This work is according to our knowledge the first tentative to carry out the oxybutylation of tannins in order to develop fully based aromatic polyols. Different condensed tannins (Table 1) were selected for this study and the corresponding results were compared. The purpose of this study was to enhance the reactivity of tannins by modifying their original structures. Phenolic OH groups were converted into grafted polyether aliphatic chains with active OH end groups (Fig. 1), for future reactions.[5] This study is focused on the analysis of the influence of the main parameters of the synthesis in connection with the characterization of the ensuing polyols. Different series of polyols were synthesized with different (T/BO) mass ratios (w/w). Catalyst content was kept constant. The first part of this paper is concentrated on the optimization study applied to gambier tannin. In the second part, the impact of the botanical origin on the resulting macropolyols was evaluated. All resulting polyols were fully characterized by infrared spectroscopy (FTIR), ^{1}H and ^{31}P NMR spectroscopy, thermogravimetric

analysis (TGA), differential scanning calorimetry (DSC), viscosimetry, size exclusion chromatography (SEC) and OH number analysis.

2. Experimental

2.1. Materials

Various condensed tannins used in this work were kindly supplied by Silva Chimica (St. Michele Mondovi, Italy). They were extracted from Gambier (*Uncaria gambir*, GT) located in Indonesia, Mimosa (*Acacia mearnsii*, MT) located in Tanzania and Quebracho (*Schinopsis balansae* and *Schinopsis lorentzii*, QT) located in Argentina and Paraguay. Pine tannins (PT) were supplied by DRT (France), from maritime pine (*Pinus pinaster*) located in the south of France. GT, MT and PT are hot water extracted, whereas QT are obtained by a sulfite process extraction.

BO, potassium hydroxide (KOH), dichloromethane, anhydride pyridine, cyclohexane were purchased from Sigma Aldrich and used as received. For NMR analysis, deuterated chloroform ($CDCl_3$), deuterated dimethyl sulfoxide (DMSO-d_6), pentafluorobenzaldehyde (PFB), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), cholesterol and Chromium (III) acetylacetonate were also purchased from Sigma Aldrich and used as received without further purification.

A list of the acronyms used in this paper is presented in ESI.

2.2. Chemical modifications

2.2.1. Tannin acetylation

Acetylation is commonly used to increase the solubility of lignins in organic solvent, in order to analyze their respective complex structures namely for SEC analysis.[26, 27] Such a strategy can be applied to tannins.[17] 1 g of dry neat tannin was acetylated in 20

mL mixture of acetic anhydride/pyridine (1/1, v/v) at room temperature for 24 h in a 50 mL round-bottom flask. After 24 h, 5 mL of methanol were added to quench the remaining acetic anhydride and 40 mL of dichloromethane were added to solubilize the product obtained. The resulting solution was first washed with hydrochloric acid solution (2 M). Next, the corresponding organic layer was washed with a saturated sodium bicarbonate solution to eliminate acetic acid, and finally washed with deionized water to remove any residual salts. The dichloromethane solution was dried with anhydrous sodium sulfate and the product was evaporated under reduced pressure. Acetylated tannin was finally dried under vacuum at 35 °C, overnight.

2.2.2. Oxybutylation reaction

Only few publications were issued about oxybutylation which is a ring-opening polymerization (ROP) of BO through OH groups (Fig. 1). [28, 29] BO is more hydrophobic and gives less transfer reactions than PO.[30, 31] This advantage is due to a decrease in the acidity of the hydrogen atoms of the methyl group from the ethyl substituent of BO, compared to those of methyl substituent of PO linked to the carbon of the oxirane ring.[32] Oxybutylation could be catalyzed by alkaline catalyst and KOH is a conventional catalyst for this reaction.[28] Under alkaline condition, monoalkyl-substituted epoxides react predominantly on the less substituted carbon, due to the steric effects.[32] This reaction is defined as a bimolecular nucleophilic substitution (SN_2 type reaction) (Fig. 2).

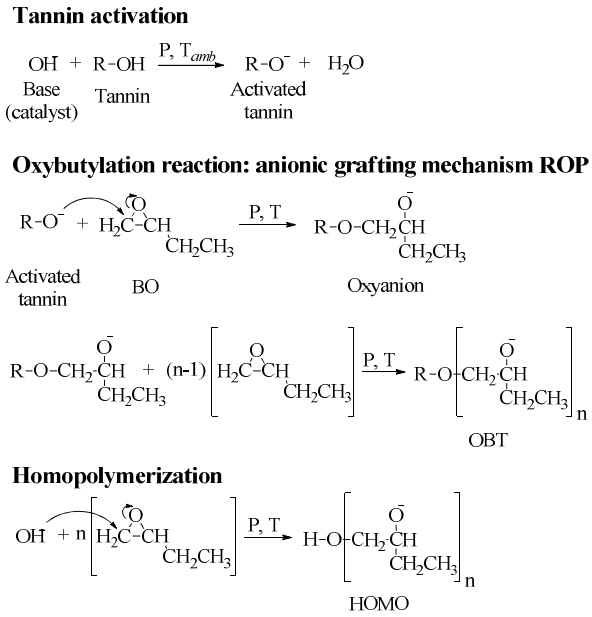


Fig. 2. Schematic representation of the oxybutylation reaction mechanism with: tannin activation, anionic grafting reaction and homopolymerization steps.

The initial activation of the tannin is due to the reaction with KOH (Fig. 2). The first BO addition gives the formation of an oxyanion. Then, the propagation by polymerization of BO can take place to synthesize an aromatic polymer with poly(butylene oxide) (PBO) grafted chains. Unfortunately, BO aliphatic homopolymer (HOMO) composed of free PBO was also obtained as a by-product.[32, 33] Thus, the resulting polyol was a mixture of oxybutylated tannins (OBT) and HOMO.

The oxybutylation reaction was carried out in a 600 mL pressure reactor (Parr, model N°4568) equipped with a heating mantle, a mechanical stirrer, a thermocouple and a manometer. Tannin, BO and KOH (fine powder form) were introduced in the reactor, which was then closed and heated up to 150 °C, under stirring. As a result, an increase in temperature and pressure was observed until a maximum temperature and pressure, T_{max} and P_{max}, respectively. These values are dependent on the amount of tannin. The pressure then decreased almost instantaneously after the complete consumption of BO.

When the pressure returned to almost zero, the reaction was considered to be complete. The reactor was cooled while stirring and the ensuing tannin-based macropolyol was extracted. This polyol was then dissolved in dichloromethane to enable the purification.

This purification of OBT was performed following a two-step process. First, the residual KOH was removed and then HOMO fraction was extracted. To eliminate KOH, the organic layer was washed several times with brine until the pH was neutralized. Then, the organic layer was dried on anhydrous sodium sulfate, filtered and the corresponding filtrate was evaporated by rotary vacuum. The so-obtained polyol mixture was dried under vacuum at 35 °C overnight. The HOMO fraction was separated from the tannin-based polyol mixture for characterization purposes and also to evaluate their relative influence on the final polyol mixture. HOMO were removed by extracting twice the polyol mixture with cyclohexane under reflux according to the method previously established by Pavier.[34] The recovered fractions (OBT and HOMO) were subsequently dried under vacuum at 60 °C overnight, to remove cyclohexane residue. Both fractions were weighted to determine the HOMO content in the polyol mixture.

All reactions were carried out with 100 mL of BO. The corresponding designation for the synthesized polyols is T/BO, where T/BO is the mass ratio between tannin (GT, PT, QT or MT) and butylene oxide. Four series of polyols were synthesized with T/BO ratios of 40/60, 30/70, 20/80 and 10/90 (w/w), respectively.

2.3. Characterization techniques

FTIR analysis

Spectra were recorded on a Nicolet 380 FTIR spectrometer in the range of 4000 and 400 cm^{-1}, with an accumulation of 16 scans. It was used in Attenuated Total Reflectance Mode (FTIR-ATR).

Quantitative ^{1}H NMR analysis

Spectra were recorded using a Bruker UltraShield 400 MHz at room temperature to estimate the degree of polymerization of BO on tannin.[15] A standard solution of PFB in DMSO-d_6 was prepared by weighting 33 mg of PFB diluted in 0.40 mL of DMSO-d_6. 20 mg of OBT was dissolved into 800 µL. An aliquot of the standard solution (0.10 mL) was added. The solution was then transferred into a 5 mm NMR tube. The relaxation delay was set to 10 s with 32 scans.

Quantitative ^{31}P NMR analysis

Spectra were acquired using a Bruker 400 MHz equipped with a "Quad probe" dedicated to ^{31}P, ^{13}C, ^{19}F and ^{1}H NMR acquisition. A relaxation delay of 10 s was used, and the number of scans was 512. Samples were prepared according to previous procedures.[35, 36] A solvent solution of anhydrous pyridine and $CDCl_3$ (1.6:1, v/v) was first prepared. It was used for the preparation of the relaxation reagent (Chromium (III) acetylacetonate, 5 $mg.mL^{-1}$) and the internal standard solutions (Cholesterol, 0.1 M). Approximately 10 g of tannin or OBT was dissolved in 400 µL of the solvent solution, followed by the addition of 100 µL of the internal standard and relaxation solutions, respectively. Finally, the mixture was treated with 100 µL of phosphitylating reagent (TMDP). Samples were stirred at 20 °C for 90 min, and then were transferred into a 5 mm NMR tube for subsequent analysis. The reaction of TMPD with OH groups is illustrated in Fig.3. TMDP reacts with OH functional groups to give phosphite products which are resolvable by ^{31}P NMR into separate regions arising from aliphatic and phenolic hydroxyl groups.

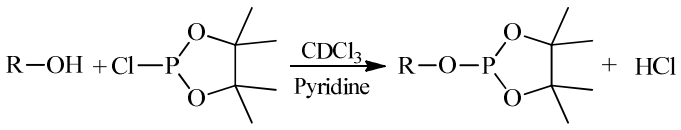


Fig. 3. Reaction of TMPD with OH groups.

SEC analysis

SEC analysis were performed in THF (HPLC grade – 1 mL.min^{-1}) using a Malvern Instrument liquid chromatograph. The setup consisted of a thermostated oven with a 8 µ guard column and three 6 µ 300 mm-columns (50, 150 and 500 Å), followed by two online detectors: a refractive index (RI) detector (VE 3580 RI Detector) and a UV detector (UV Detector 250). Average molar masses and dispersity (Đ) were determined using polystyrene (PS) as a standard from 162 to 20,000 g.mol^{-1}. Samples were dissolved in THF (5 mg.mL^{-1}) and filtered through a 0.2 µ polytetrafluoroethylene membrane.

Hydroxyl index (I_{OH})

I_{OH} is a key parameter in the characterization of polyols. This value is the amount of KOH, in milligrams, equivalent to the OH content of 1 g of polyol. I_{OH} was determined by the standard esterification method using phthalic anhydride.[7] Polyol (2 g) and the pthalation reagent (20 mL) were heated at 115 °C for 45 min, cooled to room temperature. Pyridine (30 mL) was then added, followed by water (30 mL). The solution was then titrated with a 1.0 M sodium hydroxide (NaOH) solution. The phthlation reagent was a 1.0 M solution of phthalic anhydride in pyridine. Hydroxyl index (I_{OH}), in mg of KOH.g^{-1}, was determined according to Eq. (1):

$$I_{OH} = \frac{(V_{blank} - V_S) \times C \times 56.1}{W_S} \quad (1)$$

V_{blank} (mL) and V_S (mL) are the volumes of NaOH solution required for blank and polyol sample titrations, respectively. C (mol.L^{-1}) is the NaOH solution concentration and W_S (g) is the polyol weight. In case of neat tannins, the phthlation reagent was a 1.0 M solution of phthalic anhydride in pyridine with imidazole (1.5%) and the reaction

time was 5 hours, because of their lower reactivity compared to oxybutylated derivatives.

TGA analysis

TGA was used to determine tannin thermal stability by monitoring sample weight loss as a function of temperature. TGA was carried out on a Hi-Res TGA 2950 apparatus from TA Instruments. Samples were heated from 25 up to 700 °C under dry nitrogen at a constant heating rate of 10 °C.min^{-1}.

DSC analysis

DSC thermograms were performed using a TA DSC Q200 calorimeter, at a constant rate of 10 °C.min^{-1} under nitrogen atmosphere. Samples were heated from 25 up to 120 °C, cooled to -80 °C, and then heated again up to 120 °C. The glass transition temperature (T_g) was determined at the midpoint of the change in the baseline slope of the second heating cycle.

Viscosity analysis

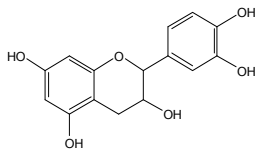
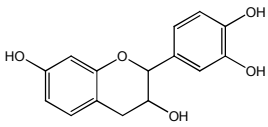
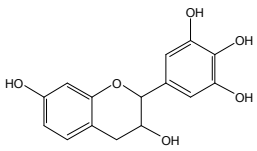
Polyol viscosity was determined at 30 °C with a stress-controlled Bohlin Gemini rheometer (Malvern Instruments, UK), with cone-plate geometry (4°) presenting a 20 mm diameter.

3. Results and discussion

3.1. Tannins characterization

Depending on the species, tannins present variations in the chemical structure, as shown for instance by Table 1. These condensed tannins are oligomers based on flavonoid units, composed of two phenolic rings (A and B rings) linked by a heterocyclic ring (Fig. 1).

Table 1. Main characteristics of tannins.

Tannin	**Gambier** (GT)	**Pine** (PT)	**Quebracho** (QT)	**Mimosa** (MT)
Chemical structure	Procyanidin 		Profisetidin 	Prorobinetidin 
Linkage	4-8		4-6	4-6
Degree of polymerization	Low	Medium	High	High

GT and PT are both mainly composed of procyanidins units (phloroglucinol A-ring, catechol B-ring). Each procyanidin unit is mostly 4,8-linked with lower degrees of polymerization for GT (50% monomeric) than other tannins [37, 38] *e.g.*, PT is a mixture of oligomers (trimers and tetramers).[39] QT (profisetidin) and MT (prorobinetidin) possess higher degree of polymerization.

Each tannin chemical structure needs to be precisely determined since its main characteristics depend on its botanical sources. Total and aromatic OH contents were quantified according to different techniques. Chemical titration, ^{1}H NMR based on acetylated tannin and quantitative ^{31}P NMR were carried out. These techniques gave access to I_{OH} and to the nature of OH groups (phenolic vs. aliphatic).[36] To perform ^{31}P NMR, tannins were modified with a phosphitylating reagent to a phosphorus atom. Similar characterization methods were previously reported for neat and modified lignins.[10, 40, 41] The polyols were analyzed using a specific procedure for tannins, based on NMR characterizations.[36]

In the case of tannins used in this study, the I_{OH} obtained by titration depends of the botanical source (Table 2). By titration, I_{OH} values are between 630 and 857 mgKOH.g^{-1}. These values are in the same range as, for example, 900 mgKOH.g^{-1} which was recently obtained on green tea tannins.[7] By ^{1}H NMR analysis, aromatic and aliphatic acetates gave signals, at 2.3 and 2.1 ppm, respectively (see ESI). These peaks

are related to aliphatic and phenolic OH groups present in tannin before acetylation. Except for PT, tannins have more phenolic OH groups than aliphatic ones.

Table 2. Chemical characterizations of the different tannins.

	Tannin	GT	PT	QT	MT
Titration Acetylation	I_{OH} (mgKOH.g^{-1})	630	857	654	793
	Aliphatic OH (%)	34	70	39	38
	Phenolic OH (%)	66	30	61	62
^{31}P NMR	I_{OH} (mgKOH.g^{-1})	747	928	638	844
	Aliphatic OH (%)	36	72	33	37
	Phenolic OH (%)	64	28	97	63

These results are in good agreement with those obtained by ^{31}P NMR analysis (Table 2). By this method, I_{OH} were compromise between 747 and 928 mgKOH.g^{-1}. GT spectrum is given as an example (Fig. 4).

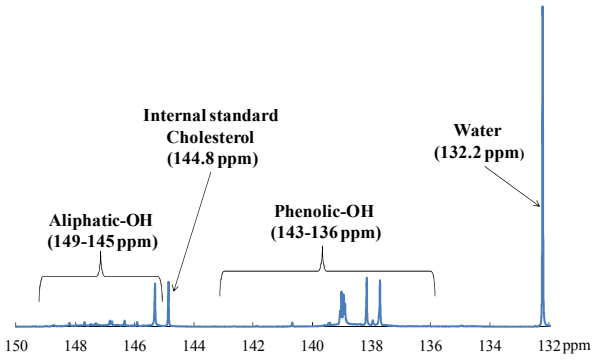


Fig. 4. ^{31}P NMR spectra of GT.

Two broad regions: aliphatic region (149-145 ppm) and phenolic region (143-136 ppm) can be easily distinguished. As previously obtained using the titration method, the percentage of each type of OH depends on the nature of tannins (Table 2). Results close to those found in this study have already been observed for grape seeds and grape wood tannins.[36]

3.2. Synthesis and characterization of oxybutylated gambier tannin (OBGT)

The first part of this study focuses on synthesis using only one type of tannin, namely gambier. After oxybutylation of the GT, the resulting mixture (OBGT and HOMO) is brown, viscous and fully soluble in solvent media.

According to Table 3, P_{max} was kept almost constant between 7.0 and 7.8 bar, regardless of the GT/BO ratio. On the other hand, T_{max} increased with the GT/BO ratio from 150 to 192 °C. At high GT content, several grafted chains grow at the same time from the numerous OH groups. Therefore, since the oxybutylation is an exothermic reaction due to the high ring strain energy of the oxirane ring, temperature increases during the reaction time.[32] Compared to the oxypropylation on tannins, it is well-know that BO is less reactive than PO. Thus, for BO there are no exothermic temperature peaks for 20/80 and 10/90 ratios.[32] The reaction time is longer for oxybutylation compared to oxypropylation,[42] and it decreases with the increase in GT content.

Table 3. Operating conditions and main parameters for the synthesis of tannin-based polyols.

Tannin	T/BO (w/w)	T_{max} (°C)	P_{max} (bar)	Reaction time (min)
GT	**40/60**	192	7.8	107
	30/70	169	7.0	130
	20/80	150	7.0	274
	10/90	150	7.6	1476
PT	**30/70**	178	7.7	236
MT	**30/70**	174	7.7	123
QT	**30/70**	150	7.6	n.a.

All GT-based polyols were analyzed by FTIR analysis to control the grafting. FTIR spectra of neat GT and of polyol mixture (case of 20/80 polyol) were presented in ESI. The corresponding polyol mixture revealed an increase in the IR bands in the range of 2870-2970 cm^{-1} and 980-1200 cm^{-1} attributed to the stretching mode of -CH-, -CH_2- and

-CH_3 aliphatic groups and to -CO- stretching region associated with ether moieties, respectively. Moreover, the substantial increases in the band at 1462 cm^{-1}, relating to -CH_2- and -CH_3 groups deformations, prove the success of the PBO chain grafting.

HOMO content evolution of polyol mixture is similar with previous works based on oxypropylation of GT [42] and with previous works based on other types of biomass.[12, 13, 34] In Table 4, the results show that the formation of HOMO decreased with the increase in the GT/BO ratio. In a previous study on sugar beet pulp oxypropylation, SEC analyses have shown that the soluble fraction was mainly composed of HOMO and the insoluble fraction was composed of oxypropylated biomass.[34] This method was also used on oxypropylated tannin.[42] However, for polyols from 10/90 and 20/80 series, HOMO cannot be isolated. Consequently, the HOMO content cannot be precisely determined because OBGT is soluble in cyclohexane phase. This is probably due to the long grafted chains which increase the OBGT solubility in cyclohexane.

Table 4. Main characterization of the resulting tannin-based polyols (HOMO content, viscosity at 30 °C, I_{OH}, T_g, average-molar masses and Đ).

Tannin		GT				PT	MT
T/BO (w/w)		40/60	30/70	20/80	10/90	30/70	30/70
HOMO content (%)		5.5	32.0	-	-	33.5	12.2
Viscosity of mix[a] at 30 °C (Pa.s)		-	15	4	1	253	57
I_{OH}[b] (mgKOH.g^{-1})	Mix	370	316	241	142	352	327
	OBT	365	328			295	326
DSC results	T_g mix (°C)	1	-41	-54	-62	-40	-38
	T_g HOMO (°C)	-22	-56	-	-	-62	-62
	T_g OBT (°C)	24	11	-	-	-1	-9
SEC results	M_n OBT (g.mol^{-1})	1600	2100	2420*	3980*	4820	3470
	M_w OBT (g.mol^{-1})	3030	4210	4930*	7140*	29,000	6,800
	Đ OBT	1.9	2.0	2.0*	1.8*	60.0	2.0
	M_n HOMO (g.mol^{-1})	190*	260	390*	740*	310	350
	M_w HOMO (g.mol^{-1})	240*	290	440*	900*	330	380
	Đ HOMO	1.2*	1.1	1.1*	1.2*	1.1	1.1

[a] mix: polyol mixture
[b] Determined by chemical titration
[c] According calculations based on Eq. (2)
* Results obtained from mixtures.

SEC analysis was performed on acetylated GT, on the original polyol mixture and on each fraction (OBGT and HOMO fractions). The molar mass distributions were determined by RI detection. The elution volume of each compound was attributed through UV mode in which only OBGT distribution was observed due to its aromatic structure. Fig. 5(a) showed the different elution profiles for acetylated GT and 40/60 polyol using RI detection with different elution times. HOMO fractions were obtained at 24 and 26 min (Fig. 5(a) box 1) and OBGT between 17 and 23 min (Fig. 5(a) box 2), respectively. The major structure in acetylated GT is probably the acetylated monomeric procyanidine corresponding to the peak at 24 min (Fig. 5(a)). After oxypropylation

process, this peak disappeared due to the OBGT molar mass increase due to the grafted chains.

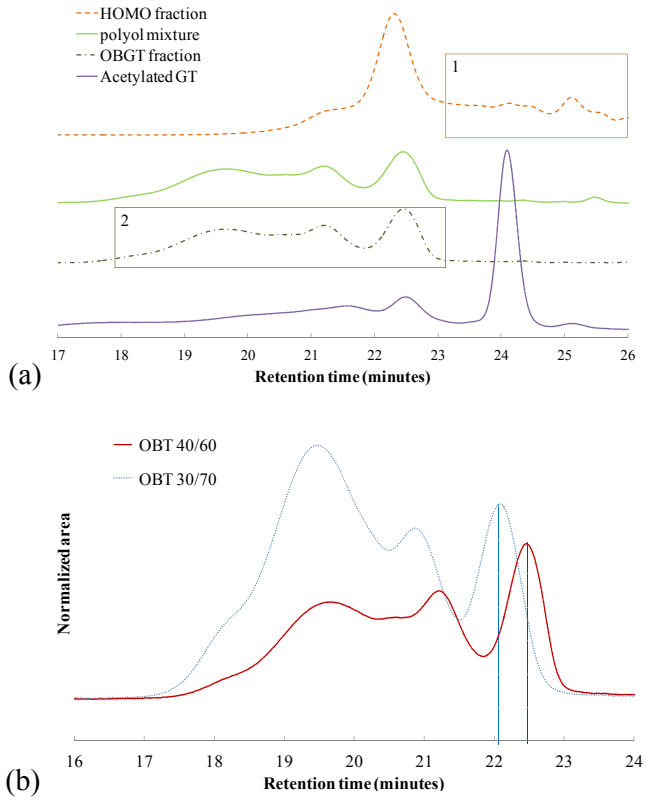


Fig. 5. SEC profiles with RI detection (a) obtained for acetylated GT and for polyol mixture, HOMO and OBGT fractions of 40/60; (b) as a function of GT/BO ratio.

The elution profiles showed the limited efficiency of the fractionation procedure due to the presence of HOMO traces in OBGT. In the same way and even to a larger extent, the HOMO fraction still contained a non-negligible content of residual OBGT. Nevertheless, it was possible to compare the different series based on OBGT polyols. Other solvents were tested to obtain a superior separation. For the moment, cyclohexane gave the most satisfying results. When the GT/BO ratio decreases *i.e.*, when a small excess of BO was introduced (Fig. 5(b)), elution profile shifted towards shorter

retention times resulting in an increase in the hydrodynamic volumes. Therefore, the results suggested the formation of shorter grafted chains for high GT/BO ratios (60/40 and 70/30 series).

All the polyols viscosities were measured except for the polyols of the 40/60 series because of their solid state (Table 4). The viscosity evolutions are in agreement with previous observations. The viscosities increased with the GT/BO ratios. This trend resulted from the diminution of HOMO content with the increase in GT content. Moreover with the increase in GT/OB ratios, more viscous OBGT were obtained due to shorter grafted chains which brought less mobility than long chains. The increase in the mobility can also be observed through the T_g evolution of polyol mixture (Table 4). Neat GT did not show detectable T_g. For polyol mixtures, in the case of series with low GT content such as 10/90 and 20/80, the presence of higher HOMO content led to lower T_g values since HOMO acts as a plasticizer, as previously mentioned. Concerning OBGT fractions, T_g depended on the GT/BO ratio. The T_g increased with GT content. This increase was due to the strengthening linked to the tannin backbone. The T_g of the HOMO fraction of 30/70 series was close to those of the poly(1,2 butylene) glycol at 500 $g.mol^{-1}$, which is -56 °C. In the case of 40/60 series HOMO fraction, T_g is higher. As previously observed with SEC analysis, they were some OBGT polyol traces in HOMO fraction, which were responsible for the increase in T_g.

OH indexes of the polyols were found to be between 140 and 370 $mgKOH.g^{-1}$ (Table 4). These values are close to those obtained for fossil-based polyols used industrially in the synthesis of polyurethanes.[32] For all polyols, the I_{OH} values were low compared to the initial GT (630 $mgKOH.g^{-1}$). This reduction is linked to the increase in the molar masses by grafted polymerization. The I_{OH} values which are per gram of

polyol, are inversely proportional to M_n. I_{OH} values increase with the GT/BO ratio. Similar results were previously observed for other alkoxylated biomasses.[12, 13, 42]

GT and oxybutylated polyol derivates were analyzed by TGA. TGA curves of 30/70 series were presented on Fig. 6. The results show that no degradation occurred during DSC analysis in the corresponding explored temperature range. The mass loss between 0 and 150 °C can be attributed to the vaporization of linked and non-linked water. The tannin decomposition started at 150 °C with a pyrolytic degradation in a one-step mechanism. A unique peak appeared in the DTG curve at 270 °C. At higher temperature, there was a gradual decrease in sample weight which led to a great amount of residual mass (around 40% at 700 °C). Similar results have been reported on pine bark tannins that have suggested that polysaccharide contents influenced the degradation temperatures.[43] For high carbohydrate contents (>10%), the degradation temperature decreased in comparison with pure tannin. However, if this content is low, pine bark tannins present a degradation temperature at around 200 °C. From these observations and in our case, the obtained results suggest that the purity of GT is high due to the high degradation temperature (270 °C).

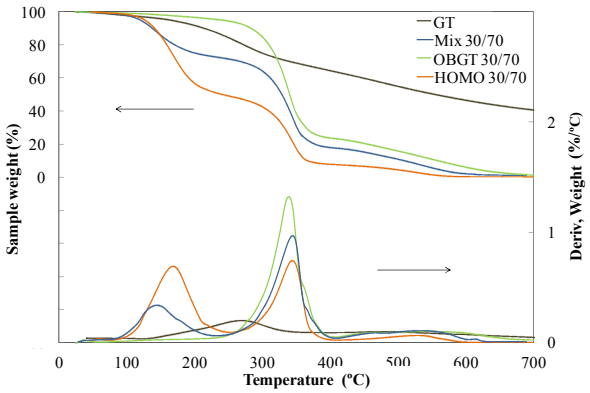


Fig. 6. TGA/DTG curves of GT, of the 30/70 polyol mixture and the corresponding HOMO and OBGT fractions, under nitrogen atmosphere.

Tannin derivatives showed lower thermal stability due to the degradation of grafted polyether chains, linked to the thermal sensitivity of ether groups.[44] However, in the case of lignin, some authors have shown that thermal stability of lignin was improved by the selective masking of phenolic hydroxyl group by methylation or oxypropylation.[16] This was also the case for tannins up to 330 °C. Past this temperature, OBGT showed lower thermal resistance compared to neat GT due to the degradation of the PBO grafted chains. Equivalent results were previously observed for oxypropylated tannin.[42]

3.3. Effect of the botanical source

The second part of this study is based on the analysis of the variation of the botanical origin on OBT properties. Considering previous results from this study, only one T/BO ratio (30/70) was considered on other tannins *i.e.*, PT, MT and QT (Table 3). This ratio was chosen because the separation of HOMO from the polyol mixture was more efficient.

With QT, the reaction occurred only after more than 3 days. The pressure decreased until 5.8 bar after 24 h of reaction. It is known that compared to other tannins, QT is slow reacting in case of reaction with *e.g.*, formaldehyde.[45] This is due to the chemical structure of this particular tannin. In case of QT and PT, the flavanoid A-rings are composed of resorcinol whereas it is phloroglucinol for MT and QT. However, in the case of MT, the low reactivity of the A-ring is balanced by the B-ring of the pyrogalloyl (Table 1). For QT, no reactivity might be explained by the catechol B-ring. Moreover for QT, this non-reactivity is also probably due to the tannin extraction process, using sulfite, and the corresponding final chemical structure. Then, for the rest of this study, QT are no longer considered. Nevertheless, additional experiments are in process to fully understand this low or non-reactivity. For GT, MT and PT, T_{max} and P_{max} values

are close. Reaction times were equivalents for GT and MT whereas it was longer for PT. For this latter, OH accessibility is reduced compared to other tannins, owing this to its high degree of polymerization, leading to longer reaction time.

All corresponding polyols were analyzed and controlled by FTIR analysis and showed that in all cases, the grafting occurred, involving the same bands as the GT spectrum. Main results of TGA analysis were similar compared to the OBGT cases. Tannins derivatives showed lower thermal stability relative to neat tannins caused by the degradation of grafted polyether chains (see curves in ESI). Properties of polyols were summarized in Table 4. HOMO polymer content depended on the tannin type and it was around 30% for PT and GT and around 12% for MT. This can be the consequence of the chemical structure of MT, which is composed of prorobinetidin units and possesses a high degree of polymerization in comparison with GT and PT.

SEC analysis showed that residual traces of HOMO were found in OBT fractions, like previously observed in the case of OBGT. As expected, the elution profile shifted towards shorter retention times when tannin molar masses increased (Fig. 7). Thus, OBT molar masses increased with the molar masses of the neat tannins.

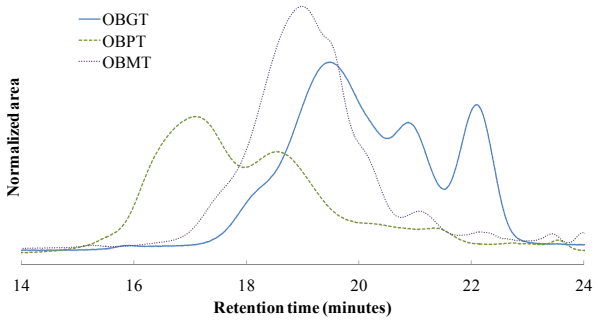


Fig. 7. SEC profiles with RI detection obtained for OBT fractions of 30/70.

Moreover, polyol mixtures presented a large range of viscosities. The viscosity increased with both the tannin molar mass and I_{OH}, and then with the number of POB grafted chains.

3.4. Study of the chemical structures of the OBT by NMR analysis

Quantitative ^{31}P NMR was carried out to monitor and characterize neat and OBT. After oxybutylation, all ^{31}P spectra showed that the phenolic OH as well as the initiate aliphatic OH groups disappeared compared to neat tannin spectrum (Fig. 4). As an example, ^{31}P spectra of OBGT 70/30 is presented in Fig 8. The large zone observed between 145.9 and 147.1 ppm was attributed to the new aliphatic OH groups due to the grafted chains formed during the oxybutylation reaction. Moreover, the spectrum showed the complete disappearance of the phenolic OH peak which proves that the tannin was fully oxybutylated.

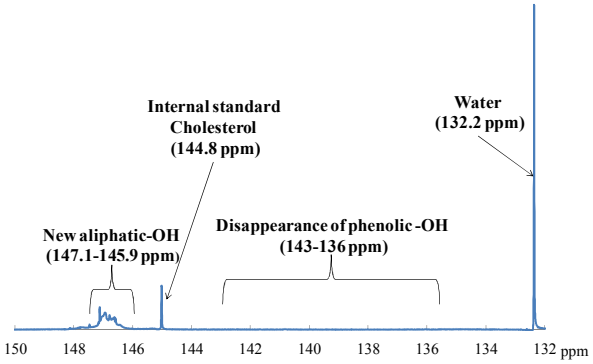


Fig. 8. ^{31}P NMR spectra of OBGT 70/30.

To estimate the average number of BO units per initial tannin OH group, quantitative ^{1}H NMR was performed following the method recently developed based on oxypropylated lignin.[15] To illustrate, Fig. 9 shows the case of 70/30 OBGT. The distinct regions were respectively attributed to the aromatic protons (8.0-6.0 ppm), methoxy protons (5.2-2.6 ppm) and the new aliphatic methyl protons of PBO grafted chains (1.4-

0.5 ppm). Quantitative ^{1}H NMR allowed a good estimation of the methyl groups insertion onto tannins via the grafted PBO chains.

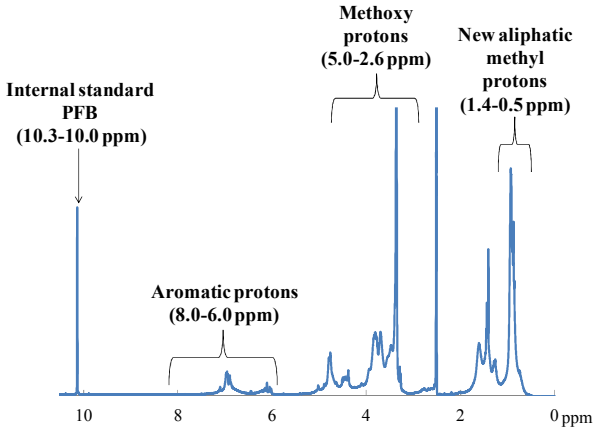


Fig. 9. ^{1}H NMR spectrum of 70/30 OBGT.

According to the ^{31}P NMR, OH group analysis and the ^{1}H NMR methyl group calculation, it is possible to calculate the average number of BO units per PBO chains grafted onto tannin. Results were found following Eq. (3) and shown in Table 5:

$$\frac{CH_3(^1H)}{OH_{aliphatic}\ (^{31}P)} = \text{number of BO units per chain} \quad (3)$$

Table 5. Results of ^{31}P and ^{1}H NMR for OBGT (40/60 and 70/30), OBPT (70/30) and OBMT (70/30)

OBT	OBGT		OBPT	OBMT
T/BO ratio	40/60	30/70	30/70	30/70
Average number of BO units per chain	1.2 ± 0.1	1.4 ± 0.1	2.6 ± 0.1	2.4 ± 0.1
Average number of chains per tannin molecule	11.3 ± 0.6	11.0 ± 0.6	25.4 ± 0.3	15.3 ± 0.8

The average number of BO units per chain depends also on the tannin. In case of GT, the average length of grafted chains slightly decreases with the increase in GT/BO. However, considering the other results such as SEC and viscosity measurements, longer

chains were synthesized in case of 30/70 compared to 40/60. The relative order concerning the average number of BO units per chain was PT > MT > GT, the last one presenting the lowest values. This was due to the number of present OH groups during the oxybutylation process: if less OH groups were introduced, the average number of BO units per chain (for a constant content of BO) would have been higher. Mass ratios were used in this study and consequently, molar ratios of T/BO were different according to the used tannin. Thus, in case of PT, molar ratio of PT/BO as well as the number of OH groups were the lowest.

Using HOMO content previously determined, it was possible to evaluate the average number of grafted chains per tannin molecule (Table 5). The number of chains varied from 11, 15 and up to 25 for GT, MT and PT, respectively. This value depends only on the chemical structure of tannin used for the oxybutylation and showed that the tannin botanical source has a great impact on the OH functionality for the OBT obtained. Indeed, in case of GT, the number of chain per tannin molecule was constant at around 11 regardless of the ratio. This result also proved that all OH have reacted with the OB and was also found in case of oxypropylation.[42]

4. Conclusion

During this study, different tannin-based macropolyols, from various botanical sources have been successfully synthesized and then fully characterized. Four different types of tannins have been analyzed and tested. First, GT was used to find the best reaction conditions varying the T/BO ratio. Various analysis methods were used to prove that high tannin content induces shorter grafted chains. Moreover, lower HOMO is synthesized when GT content is high. On the contrary, for lower GT/BO ratios, *i.e.* with a large excess of BO, the formation of long grafted chains and the formation of

HOMO were favored. These conclusions are in agreement with those previously found on oxypropylation of GT.[42] OBT properties depend both on the reaction parameters and botanical source of tannins. The investigations through quantitative ^{1}H and ^{31}P NMR analyses show that (i) the PBO grafted chain length increases with the T/OB ratio, (ii) the number of PBO grafted chains per tannin molecule is mainly monitored by the botanical source and varied from 11, 15 and up to 25 for GT, MT and PT, respectively.

Thus, tannin oxybutylation process provided taylor-made, fully biobased and controlled macropolyols which can be employed for the elaboration of innovative aromatic polymers leading to new macromolecular architectures, such as polyesters or polyurethanes. These structures obtained from a green and a highly sustainable chemistry (synthesis without solvent, high renewable content) can be used for a large range of long-term applications (transportation, building …).

As perspectives of this work, the oxybutylation of other types of biomasses such as lignins must be tested to obtain aromatic macromolecular architectures, with highly biobased contents.

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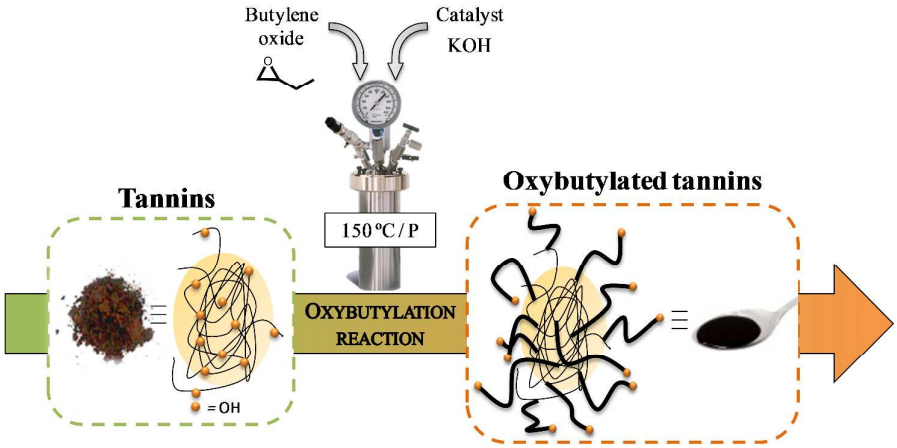

New fully biobased macropolyols obtained by oxybutylation from different tannins.