Biobased and Aromatic Reversible Thermoset Networks from Condensed Tannins via the Diels–Alder Reaction

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Supporting Information

ABSTRACT: Thermo-reversible networks were obtained for the first time from tannins, an aromatic biobased polyphenol, by reacting furan-bearing tannins and telechelic oligomers with maleimide end groups, using the Diels–Alder (DA) reaction. Condensed tannins from mimosa (Acacia mearnsii) were functionalized with furfuryl glycidyl ether and thoroughly characterized by 1H, 31P NMR, and FTIR spectroscopy. The accessibility of the grafted furan groups was confirmed by a model reaction with N-methylmaleimide. Different cross-linked networks were then obtained by DA reaction with three PPO and PPO-b-PPO-b-PPO oligomers and evidenced by FTIR spectroscopy. The thermal properties of the obtained networks were evaluated with differential scanning calorimetry (DSC) and thermogravimetric analysis. Then, the reversibility of the cross-linking was shown by a quick return to the liquid state upon heating at 120 °C. The retro Diels–Alder reaction was studied by size exclusion chromatography and DSC.

KEYWORDS: Tannins, Diels–Alder, Retro Diels–Alder, Cross-linking, Biobased

INTRODUCTION

With the increasing lack of certain fractions from fossil resources, the subsequent price volatility, and an increasing pressure from the civil society for a more sustainable industry, researchers, and among them chemists, are urged to find alternatives to fossil-based derivatives. Biobased aromatic derivatives are especially sought, since BTX (benzene, toluene, xylene) fractions from naphtha are nowadays less and less available due to the strong increase in global demand. However, aromatic monomers are largely used in polymer materials for their rigidity and chemical and thermal stability, as well as their ability to structure the matter by π-stacking, thus providing high performances. Finally, biobased aromatic derivatives can also bring some new chemical architectures.

Among the aromatic biobased compounds, tannins appear as interesting candidates in the field of materials chemistry. After lignins, they are the second most abundant natural source of phenolic derivatives.1 They are found in the soft tissues (sheets, needles, or bark) of all vascular plants and exhibit various functions and nucleophilic sites may easily lead to various functionalizations.1 For all these reasons, tannins or their depolymerized building units have been successfully used in the synthesis of polyols,6 epoxy resins,9,10 acrylate resins,14,15 adhesives,1 or foams.16–20

An important concern in polymer science, especially with thermosets, is to obtain reversible cross-linking bonds. Indeed, chemically cross-linked networks cannot be recycled by heating. Thus, a reversible cross-linking that allows depolymerizing the network is a desirable feature for an easy valorization at the end of life of the materials.21 It may also be a route toward stimuli-responsive, shape memory, or self-healing materials.22–25 Various parameters have been used to trigger the cross-linking/uncross-linking reactions such as temperature, radiations, pH, or processing.26 Among them, temperature is often seen as the easiest to apply, especially for industrial applications.27 Several systems can be used to form reversible covalent bonds with temperature including urethane or ester bonds, nitroso or azlactone groups, ionene formation, and Diels–Alder reaction. The Diels–Alder (DA) [4 + 2] cycloaddition involves a diene and a dienophile reacting to...
yield a substituted cyclohexene, which can be broken by further increasing the temperature via the retro Diels—Alder reaction (rDA). The furan—maleimide system exhibits relatively low reaction temperature for DA and rDA, around 60—70°C and 110—120°C, respectively, making it compatible with the thermal stability of most polymeric materials.

In this study, we first designed original furan-bearing tannins via the reaction of mimosa (Acacia mearnsii) tannins with furfuryl glycidyl ether in various ratios. These new functionalized tannins were characterized by spectroscopic techniques (1H and 31P NMR and FTIR) and size exclusion chromatography (SEC). Then, the accessibility of the grafted furan groups was evidenced by the study of the DA and rDA reactions with N-methylmaleimide. Original biobased networks were finally prepared with three different bismaleimide cross-linkers based on telechelic oligo(propylene oxide) and oligo(ethylene oxide).

The efficient synthesis of the DA adducts and the reversibility of the networks was finally evidenced by different techniques such as 1H NMR spectroscopy at high temperature, FTIR, SEC, and differential scanning calorimetry (DSC).

**EXPERIMENTAL SECTION**

**Materials.** Condensed tannins from mimosa (MT, Acacia mearnsii, Fintan OP) were kindly supplied by Silva Chimica (St. Michele Mondovi, Italy). Prior to analysis, they were dried in an oven at 70°C for one night and stored in a desiccator. Pyridine (sequencing grade, ≥99.5%) was purchased from Fisher Scientific, acetic anhydride (ACS reagent, ≥97%) and furfuryl glycidyl ether (FGE, 97%) from Acros Organics, and methanol (laboratory reagent grade, ≥99.9%), dichloromethane (puriss., ≥99.9%), DMSO-d6 (99.9% D atoms), and CDCl3 (99.8% D atoms) from Sigma-Aldrich.

**Syntheses. Reaction of Tannins with Furfuryl Glycidyl Ether (FGE).** Mimosa tannins (MT) were dissolved in water containing NaOH (1 mol equiv to total phenolic OH in tannins). After 30 min of stirring, FGE (from 0.25 to 1.5 mol equiv to total phenolic OH in tannins) was added dropwise, and the reaction mixture was stirred overnight at room temperature. The solution was then acidified to precipitate the functionalized tannins, down to pH ranging from 5 to 1. The precipitate was recovered by centrifugation, washed three times with 50 mL of acidified water (same pH as the precipitation pH), and freeze-dried.

**Acetylation.** Acetylation was performed in a pyridine/acetic anhydride mixture (1:1 v/v), as previously reported on tannin samples.6

**DA Reaction with N-Methyl Maleimide.** In a 10 mL round-bottomed flask, 0.1 g of furan-bearing MT was dissolved in 2 g of DMSO. After adding 31.2 mg of N-methyl maleimide, the mixture was heated at 70°C for 15 days under magnetic stirring. The crude product was cooled, precipitated in 40 mL of toluene, and centrifuged at 3000 rpm for 3 min. After removing the liquid phase, the brown solid was dried overnight in an oven at 40°C under vacuum (10⁻² mbar).

**DA and rDA with Bismaleimide Linkers.** In a small flask, 0.1 g of furan-containing mimosa tannins was dissolved in DMSO at 10 wt %, and a precise amount of bis-maleimide cross-linker was added. After vigorous stirring, the mixture was heated at 70°C in an oven. The cross-linking reaction was checked daily by turning the flask upside down to control the gel formation. The rDA reaction was carried out by heating the cross-linked sample at 120°C in an oven for 1 h, thus returning the mixture to its liquid state.

**Characterizations. FTIR Spectroscopy.** FTIR spectra were recorded in the attenuated total reflectance (ATR) mode on a Nicolet 380 FTIR or a PerkinElmer Spectrum 1000 spectrometer in the range of 400—4000 cm⁻¹, as the average of 32 scans with 4 cm⁻¹ resolution. The samples were deposited on the ATR crystal and carefully pressed to ensure a good contact. The background was recorded with the empty ATR crystal in air.

**Size Exclusion Chromatography (SEC).** SEC measurements on furan-bearing tannins were performed in chloroform (HPLC grade) in a Shimadzu liquid chromatograph equipped with a 5 μL PL Gel Guard column, two PL-gel 5 μM MIXED-C and 5 μL 100 Å 300 mm-columns, two online detectors, a Shimadzu SPD-M10A diode array (UV) detector. Molar masses and dispersity were calculated from a calibration with polystyrene standards. Acetylated tannin samples were dissolved in chloroform and filtered through a 0.2 μm PTFE membrane. For all analyses, the injection volume was 50 μL, and flow rate was 0.8 mL min⁻¹. Also, the oven temperature is set at 25°C.

SEC evidencing the rDA reaction was recorded using a triple detection SEC from Agilent Technologies. The system used two PL1113—6300 ResiPore 300 mm × 7.5 mm columns with DMF as the eluent at a flow rate of 0.8 mL min⁻¹. The detector suite comprised a PL0390—605390 LC light scattering detector with two diffusion angles (15° and 90°), a PL0390—06034 capillary viscometer, and a 390-LC PL0390—0601 refractive index detector. The entire SEC system was thermostated at 35°C. PMMA standards were used for the calibration.

**1H NMR.** Spectra were acquired on a Bruker 400 MHz spectrometer (10 s delay, 32 scans) at room temperature or 100°C for the rDA characterization. An accurately weighed amount of sample (about 20 mg) was dissolved in 500 μL of deuterated solvent. For the neat samples, DMSO-d6 was used, whereas the acetylated tannins were analyzed in CDCl3. For NMR titration, a precise amount of sample and external standard were weighed: 2,3,4,5,6-pentfluorobenzaldehyde or 2,4,6-trimethylphenol for furan or maleimide determination, respectively.

**31P NMR.** 31P NMR was performed after phosphitylation of the samples, according to standard protocols.51 The spectra were measured on a Bruker 400 MHz spectrophotometer, with 128 scans.
and a 15 s relaxation delay. Peaks assignations were performed based on previous studies on tannin model compounds.\textsuperscript{32,33}

Thermal Characterizations. Thermogravimetric analyses (TGA) were carried out on a TGA 51 apparatus from TA Instruments, from room temperature to 700°C, at a heating rate of 10°C min\textsuperscript{−1} under nitrogen flow. Differential scanning calorimetry (DSC) analyses were performed under an inert atmosphere with a calorimeter DSC1 from Mettler Toledo. All the samples were heated from −60 to 190°C at a heating rate of 10°C min\textsuperscript{−1} and then cooled to room temperature for 1 h prior to a second run.

\section*{RESULTS AND DISCUSSION}

\textbf{Grafting of Furan Groups onto Mimosa Tannins (MT).} MT were reacted with FGE to obtain a multifunctional furan-containing polymer (Scheme 1). The reaction was conducted with various amounts of FGE, ranging from 0.25 to 1.5 equiv to total phenolic OH in tannins, and the product was recovered and purified after an acidic precipitation. The reaction consumes phenolic OH groups and creates new aliphatic OH groups, as a result of the opening of the oxirane ring. Similar reactions conducted on lignin showed that under these reaction conditions only secondary aliphatic OH groups are created,\textsuperscript{34} i.e., that the nucleophilic attack of the epoxy ring by the phenolate anion only takes place at the less hindered carbon.

The content in OH of the modified tannins was measured by \textsuperscript{31}P NMR on phosphitylated samples and \textsuperscript{1}H NMR on acetylated samples (Figure 1a). Figure 1 shows the content in phenolic and aliphatic OH groups depending on the amount of FGE used for the reaction. The decrease in phenolic groups attests for the successful grafting (Figure 1b). Surprisingly, the content in aliphatic OH groups does not increase significantly with the grafting (Figure 1c). The aliphatic OH content is even lower for the derivatized tannins than for the initial one. A careful study of the \textsuperscript{31}P NMR spectra of the initial tannin, shown in the Supporting Information (Figure S1), reveals the presence of carbohydrate impurities, which give rise to some signal in the 147–150 ppm region.\textsuperscript{8} After the reaction, this signal disappeared, suggesting that the residual carbohydrates were lost, probably during the washing steps in water. A new well-defined peak at 146.3 ppm confirms the creation of the new aliphatic OH group, generated by the opening of the epoxy ring (Scheme 1).

Surprisingly, the values obtained with \textsuperscript{31}P NMR are always significantly lower than those measured by \textsuperscript{1}H NMR (Figure 1b and c), whereas previous studies showed a good correlation between both measurements in condensed tannins.\textsuperscript{35} Both measurements rely on the derivatization of the remaining OH groups, either with a phospholane or an acetyl group. As shown on Figure 1a, the phospholane group is much bulkier than the acetyl group, and it thus seems possible that it fails to access all of the remaining OH groups present in the derivatized tannins, leading to an underestimation.

The precise quantification of the grafted furan groups is mandatory to study the DA reaction. It can directly be obtained from the decrease in phenolic OH groups $\Delta(\phi-OH)$, taking into account the mass increase induced by the grafting (eq 1):

\begin{equation}
\text{furan content (mmol g}^{-1}\text{)} = \Delta(\phi-OH) + \text{mass increase induced by grafting}.
\end{equation}

\begin{table}
\centering
\caption{Content in OH and Furan Groups in Derivatized Tannins Measured with \textsuperscript{31}P and \textsuperscript{1}H NMR}
\begin{tabular}{cccccc}
\hline
name & FGE equiv & residual $\phi-OH$ (mmol g\textsuperscript{−1})\textsuperscript{a} & by $\Delta(\phi-OH)$ method\textsuperscript{b} & by direct \textsuperscript{1}H NMR method\textsuperscript{c} & average \textsuperscript{d} \\
\hline
MT & 0 & 3.72 & – & – & – \\
MT-F0.25 & 0.25 & 2.12 & 2.23 & 2.18 ± 0.05 \\
MT-F0.5 & 0.5 & 2.52 & 2.63 & 2.58 ± 0.05 \\
MT-F0.75 & 0.75 & 2.64 & 3.22 & 2.93 ± 0.29 \\
MT-F1 & 1 & 2.69 & 3.34 & 3.02 ± 0.33 \\
MT-F1.25 & 1.25 & 2.78 & 3.09 & 2.94 ± 0.16 \\
MT-F1.5 & 1.5 & 2.97 & 2.96 & 2.97 ± 0.01 \\
\hline
\end{tabular}
\textsuperscript{a}Based on \textsuperscript{1}H NMR data. \textsuperscript{b}Determined using eq 1. \textsuperscript{c}Obtained by direct integration of furan signal in \textsuperscript{1}H NMR (Figure 2).
\end{table}

Figure 1. Derivatization of OH groups with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (top) or acetic anhydride (bottom) for the quantification by \textsuperscript{31}P or \textsuperscript{1}H NMR, respectively (a), and quantity of phenolic (b) and aliphatic OH groups (c) depending on the amount of FGE used for the reaction.
where \( \Delta(\phi-OH) \) stands for the decrease in phenolic OH groups (in mol g\(^{-1}\)) and \( M_{\text{FGE}} \) for the molar mass of FGE (154.2 g mol\(^{-1}\)).

The calculation has been performed taking into account the \( \Delta(\phi-OH) \) value obtained by \(^1\)H NMR. The results are compiled in Table 1. \(^1\)H NMR was also used to directly quantify the amount of furan groups grafted to the tannins. The H atoms from the furan ring give rise to two strong signals at 6.4 (2H) and 7.6 ppm (1H) (Figure 2a). The latter was used to quantify the amount of furan groups present in each sample since it is fairly well separated from the aromatic H atoms of tannins. A good correlation between both quantification techniques is obtained. The amount of grafted furan groups quickly rises with the amount of FGE used to reach a plateau for more than 0.75 equiv.

Figure 2. Detail of the \(^1\)H NMR spectra of the initial tannin (MT) and tannin derivatized with 1 equiv FGE (MT-F1) (a) and FTIR spectra of the same (b).

FTIR was also used to evidence the successful grafting (Figure 2b). New characteristic signals assigned to the grafted FGE appear clearly: the C=O stretch around 1070 cm\(^{-1}\) or the furan ring at 740 cm\(^{-1}\). The height of this last peak is a good indicator of the grafting since it is proportional to the content in furan groups measured by \(^1\)H NMR (Figure S2, SI). In addition, a signal is detected in the C=O stretch region around 1710 cm\(^{-1}\). It was later found that its intensity increased linearly when the precipitation pH was reduced (Figure S3, SI), thus suggesting acid-induced side reactions occurring during the precipitation and/or washing steps. A similar band was observed on the neat tannin after solubilizing in water, acidifying to pH 2 and freeze-drying (Figure S4, SI). This suggests that the side reaction affects the tannin backbone rather than the grafted side chain (a putative mechanism is proposed in the SI, Scheme S1).

Precipitation and washings should then be conducted at an intermediate pH to avoid important changes in the tannin structure. However, since the recovered yield is also correlated to the precipitation pH (Figure S5, SI), a compromise has to be found. For the rest of the study, a precipitation at pH 3 was chosen.

SEC was then performed on all samples. The chromatograms are presented on Figure 3a. The derivatization causes a clear shift toward higher molar masses. The positions of the two main peaks then remain unchanged, whatever the amount of FGE used for the reaction. Increasing signal in the high molar mass region suggests possible cross-linking reactions, leading to a large increase in the weight-average molar mass \( M_w \) (Figure 3b).

All these results show that using a large excess of FGE is not necessary since it does not allow to significantly increase the grafting (Table 1) nor to ameliorate the recovered yield (Figure S6, SI). For the rest of the study, MT modified with 1.15 equiv of FGE was used unless stated otherwise.

**Model Study of DA and rDA Reaction with N-Methylmaleimide.** To study the DA reaction with furan-bearing tannins, a model reaction was carried out with N-methyl maleimide (Scheme 2). This compound has been chosen because the expected \(^1\)H NMR signal of the methyl protons in the synthesized DA adduct should not overlap with other tannin signals.

After purification, the reaction with N-methyl maleimide was characterized by \(^1\)H NMR spectroscopy (Figure 4). The success of the model reaction was confirmed by the appearance of characteristic signals of the protons of a Diels–Alder adduct at 2.9–3.0 ppm (signals k, j, and j'), 3.7–4.2 ppm (d'), and 6.5 ppm (g and g'), as well as the decrease in the signals of the furan ring at 6.4 and 7.6 ppm (e and e', and f, respectively). However, the latter did not completely disappear indicating that the reaction is not complete. The reaction time was increased up to 15 days, and the remaining furan groups were titrated via NMR by comparing signal f with 2,3,4,5,6-pentfluorobenzaldehyde as an external standard. The conversion was found to be of 50%, the DA reaction being limited, for instance, by steric hindrance.

The 3 h heating at 100 °C was not sufficient to yield the fully regenerated furan-bearing tannins, as some signals from Diels–Alder adduct are still visible, for example, at 6.5 ppm. **Cross-Linking of Furan-Bearing Tannins with Bismaleimide Oligomers.** Three bismaleimide linkers were used to cross-link the furan-bearing tannins (Scheme 3). Cross-linkers

\[ \text{Furan(mmolg}^{-1} \text{)} = 1000 \times \frac{\Delta(\phi-OH)}{1 + \Delta(\phi-OH) \times M_{\text{FGE}}} \]
X1 and X2 are telechelic poly(propylene oxide) of different chain lengths, whereas X3 is based on a poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) chain. The average degree of polymerization and precise content in

Figure 3. SEC of the derivatized tannins (a) and evolution of $M_n$ and $M_w$ with the amount of FGE used for the reaction (b).

Scheme 2. Reaction of Furan-Bearing Tannins with N-Methyl Maleimide

$^\text{a}R_1$ stands for $-\text{CH}_2-\text{CH(OH)}-\text{CH}_2$-furan and $R_2$ stands for $-\text{CH}_2-\text{CH(OH)}-\text{CH}_2$-DA adduct.

Figure 4. $^1$H NMR spectra of furan-functionalized mimosa tannins (upper spectrum) and furan-functionalized mimosa tannins reacted with N-methyl maleimide (lower spectrum) recorded in DMSO-$d_6$. $R_1 = -\text{CH}_2-\text{CH(OH)}-\text{CH}_2$-furan, $R_2 = -\text{CH}_2-\text{CH(OH)}-\text{CH}_2$-DA adduct.
maleimide groups of the cross-linkers have been determined by \(^1\)H NMR (Appendix A, SI). The results are gathered in Table 2.

### Table 2. Degree of Polymerization and Maleimide Content of Bismaleimide Cross-Linkers

<table>
<thead>
<tr>
<th>maleimide (mmol g(^{-1}))</th>
<th>degree of polymerization*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)</td>
</tr>
<tr>
<td>X1</td>
<td>5.00 ± 0.10</td>
</tr>
<tr>
<td>X2</td>
<td>3.09 ± 0.04</td>
</tr>
<tr>
<td>X3</td>
<td>1.60 ± 0.04</td>
</tr>
</tbody>
</table>

*See Scheme 3 for the meaning of \(n\), \(x\), \(y\), and \(z\).

### Table 3. Cross-Linking Experimental Conditions for Functionalized Tannins and Thermal Properties of Obtained Networks

<table>
<thead>
<tr>
<th>entry</th>
<th>cross-linker</th>
<th>maleimide:furan ratio</th>
<th>TGA</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(T_{\text{d,10%}}), (\degree\Celsius)</td>
<td>(T_{\text{fus}}), (\degree\Celsius)</td>
</tr>
<tr>
<td>XMT1</td>
<td>X1</td>
<td>1:1.02</td>
<td>298</td>
<td>400</td>
</tr>
<tr>
<td>XMT2</td>
<td>X1</td>
<td>1:1.29</td>
<td>304</td>
<td>403</td>
</tr>
<tr>
<td>XMT3</td>
<td>X1</td>
<td>1:1.73</td>
<td>256</td>
<td>408</td>
</tr>
<tr>
<td>XMT4</td>
<td>X2</td>
<td>1:1.06</td>
<td>293</td>
<td>394</td>
</tr>
<tr>
<td>XMT5</td>
<td>X3</td>
<td>1:1.04</td>
<td>347</td>
<td>399</td>
</tr>
</tbody>
</table>

*Determined by DSC during the first heating ramp; n.o. = not observed. * Determined by DSC during the second heating ramp.
cross-link density of these networks, caused by the short PPO chains (Table 2), probably caused the incomplete removal of the solvents during the drying step. On the contrary, sample XMT5 does not exhibit any degradation before 300 °C, thus indicating a very dry material because of the longer cross-linker chains, which allow an easy removal of solvents during vacuum drying.

A high char amount (from 23% to 37%) is obtained because of the stability of the phenolic tannin backbone, being greater, for example, than a cross-linked epoxy resin based on green tea tannin (21% of char at 580 °C under similar conditions). The char content decreases when increasing the cross-linker chain length as the relative content of aliphatic units in the materials is higher. Surprisingly, increasing the amount of cross-linker has little influence on the char amount (samples XMT1–XMT3,
Table 3), whereas decreasing char amounts were expected as a result of a higher aliphatic content.

The networks were then analyzed by DSC, and representative results obtained on sample XMT5 are displayed on Figure 8. During the first heating ramp, DSC thermograms exhibit two endothermic peaks around 130 and 160 °C corresponding to the rDA reaction for endo and exo adducts, respectively, as the endo adduct undergoes rDA at lower temperature. The temperatures of the rDA for endo and exo adducts are reported on Table 3. They were found to be independent of the cross-linker (128 ± 3 °C for endo and 157 ± 2 °C for exo). After 1 h cooling, a second heating ramp yields peaks with similar shape around the same temperatures, arising from an incomplete rDA reaction during the first heating step. This phenomenon is confirmed by the absence of significant exothermic signal around 70 °C during the first cooling and second heating steps, indicating that no DA adducts are formed back. Furthermore, if temperature is kept at 150 °C for 4 h after the first heating step, remaining DA adducts are still observed through the characteristic endothermic peaks during the second heating. However, the reversibility of the cross-linking was confirmed by keeping the sample at 70 °C for 6 h prior to a third heating ramp. In fact, the area of the rDA peaks was found to be higher for this last step than during the second heating step, showing that adducts were formed through DA reaction (Figure S8, SI).

The sample prepared with the longest cross-linker XMT5 is the only one to exhibit a glass transition temperature (T_g). The pristine cross-linker exhibited a T_g of −53 °C, whereas the cross-linked network has a much higher T_g of 4 °C, as measured during the first heating ramp. This is due to the presence of the aromatic backbone of MT, as well as the secondary OH groups brought by the FGE ring opening, which is reduced to −7 °C. This decrease is probably caused by the rDA that occurred during the first heating ramp: the cross-link density is lowered, causing a reduced T_g. In addition, cross-linker molecules liberated during the rDA reaction, further reducing the T_g.

The cross-linked networks are insoluble in organic solvents, as shown on Figure 9, where the sample XMT5 is immersed in a large excess of DMF. After performing the rDA during 1 h at 120 °C in DMSO, the sample became soluble and could be analyzed by SEC. After the rDA, XMT5 exhibits a sharp signal around 23.5 min and a broad signal between 14 and 23 min. The first corresponds to the free cross-linker X3, while the second has a shoulder indicating the presence of the furan-bearing tannins. The broad signal from 14 to 20 min arises from an incomplete rDA reaction (as stated by DSC) leading to soluble, but still partially cross-linked oligomers, which thus exhibit higher molar mass.

![Image](67x121 to 294x229)

**Figure 9.** Normalized refractive index (RI) response of SEC chromatograms of cross-linker X3 (red), furan-bearing tannins (blue), and crude product of XMT5 sample after rDA in DMSO. The picture on the left shows the insolubility of XMT5 in DMF prior to the rDA reaction.

**CONCLUSION**

The Diels−Alder reaction between furan and maleimide moieties was exploited to prepare new tannin-based thermo-reversible materials. In the first step, condensed tannins from mimosa (Acacia mearnsii) were modified with FGE to expose furan groups as the chain end. The reaction was confirmed by FTIR and 31P and 1H NMR. Despite a nonquantitative reaction, derivatized tannins with a high content in furan groups were obtained, up to 3 mmol g⁻¹. A model study for the reaction of furan-bearing tannins with maleimides was carried out with N-methylmaleimide. The DA reaction was evidenced by 1H NMR with a conversion reaching 50%, and its reversibility assessed with in situ 1H NMR measurements at 100 °C showing the rDA. The furan-bearing tannins were then cross-linked with three telechelic oligomers of PPO or PPO-b-PEO-b-PPO terminated by maleimide groups. The DA reaction, evidenced by FTIR, led to the formation of gels during storage at 70 °C. The gels were able to quickly turn back to the liquid state upon exposure to higher temperatures (120 °C), even though DSC and SEC experiments showed that the rDA reaction was not completed in such a short time. Finally, the obtained aromatic materials exhibited high thermal stabilities and char amounts. The use of these new multifunctional tannins and cross-linkers may open the way for tunable, partially, or fully bio-based networks with a high recycling/reuse potential for a very large range of fields such as reversible adhesive, shape memory or self-healing materials, and building, automotive, or biomedical applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02596.

31P NMR and FTIR spectra of the derivatized tannins, yields of the tannin derivatization reactions, FTIR spectra and DSC curves of the Diels−Alder cross-linked networks. (PDF)

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Notes

The authors declare no competing financial interest.

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