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Journal Name

ARTICLE

Smart Chemical Design Incorporating Umbelliferone as Natural Renewable Resource toward the Preparation of Thermally Stable Thermosets Materials Based on Benzoxazine Chemistry

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A smart synthetic chemical design incorporating a natural renewable resource, umbelliferone, is presented to synthesize thermoset materials with good thermal properties. The chemical structure of this coumarin-containing benzoxazine resin is characterized by Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectroscopy (¹H NMR). Thermal properties of the resin and its resulting thermoset are characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermoset materials are shown to have good thermal stability and a char yield higher than 55%.

Introduction,

Valorization of the biomass as an unlimited source for natural renewable raw materials to be used in the preparation of hierarchically more complex, sophisticated, and specifically designed materials to satisfy the growing needs of existing and emerging high-end technological applications is of great recent interest.¹⁻⁴ This is demonstrated by the increasing number of incentives toward this research area from scientific, governmental and industrial policies. As a result, new research fields have emerged and many others in the materials science have shifted toward a total or partial replacement of the petroleum-based materials to the biomass-based one in their products. In this regard, benzoxazines and polybenzoxazines sit on a very advantageous standpoint due to their extraordinary molecular design flexibility,⁵ which easily allows for incorporating biomass-based products into their structures⁶ thus reducing the content of the petroleum-based ones. Nature also produces a large number of phenolic and primary amine compounds that can be raw materials for the synthesis of benzoxazine resins. Given a complete set of

desirable properties exhibited by polybenzoxazines, this family of polymers is among the very few materials that has actually reached commercialization in the past 40 years. Most polybenzoxazines are still synthesized using petroleum-based starting materials; however, scientists are actively seeking for new biomass-based substitutes.^{6,7}

Briefly, the synthesis of benzoxazine resins involves three reactants, a phenolic derivative, a primary amine, and formaldehyde. Thus, incorporation of biomass-based moieties into benzoxazines can be achieved by changing the amine, or phenolic source, or both, by any comparable biomass-based derivative. In this regard, syntheses of benzoxazines exploiting natural renewable resources have been reported using, for example cardanol,⁸ urushiol,⁹ terpenediphenol,¹⁰ levulinic acid,¹¹ cinnamic/cinnamates,¹² coumarin,¹³ vanillin,¹⁴ eugenol,¹⁵ combination of guaiacol and furfurylamine,¹⁶ fluorene and furan groups,¹⁷ also placing benzoxazines as pending groups of cellulose¹⁸ or chitosan,¹⁹ in the polymer backbone,²⁰ and attached to other small molecules as thymine to induce aggregation *via* hydrogen-bonding.²¹ These examples demonstrate the increasing motivation in combining concepts from organic and polymer chemistries with materials science to purposely design and synthesize tailored monomers, smart polymers as well as enhanced and functional materials.²² These materials have demonstrated the potential to be applicable in different domains. At the same time, however, all these biomass-based benzoxazines and their respective thermosets have shown in general low thermal stability.

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Thus, motivated by these facts, we have developed a particular interest in designing a smart synthetic pathway using umbelliferone as the phenolic renewable source to synthesize a biomass-based benzoxazine for the subsequently generation of thermally stable thermoset.

Experimental

Materials

Aniline and paraformaldehyde (96%) were used as received from Sigma-Aldrich. Umbelliferone (>98%) was purchased from TCI America. PH-a was synthesized following a reported method.²³ Toluene and basic alumina were purchased from Fischer scientific and used as received.

Synthesis of 9-phenyl-9,10-dihydro-2H,8H-chromeno[8,7-e][1,3]oxazin-2-one (abbreviated as U-a).

In a 50 mL round-bottomed flask equipped with magnetic stirrer, aniline (1.49 g, 16 mmol), umbelliferone (2.59 g, 16 mmol), paraformaldehyde (1.05 g, 35.2 mmol) and toluene (22 mL) were added and stirred at reflux for 14 h. As the reaction mixture cooled, the raw product precipitated into white-yellow crystals. Finally, recrystallization from toluene yielded white needle-like crystals (Yield: 65%). ¹H NMR (600 MHz, CDCl₃, 20 °C) δ, ppm: 7.59 (d, 1H, Ar-CH=CHR (H4c)), 7.27 (t, 2H, (Hb)), 7.22 (d, 1H, (H7)), 7.14 (d, 2H, (Ha)), 6.95 (t, 1H, (Hc)), 6.75 (d, 1H, (H8)), 6.23 (d, 1H, Ar-CH=CH-COOR (H3c)), 5.43 (s, 2H, Ar-O-CH₂-NR (H2)) and 4.81 (s, 2H, Ar-CH₂-NR (H4)). FT-IR ν (cm⁻¹): 1716 (C=O str.), 1433 (CH₂ sciss.), 1360 (aromatic C-N str.), 1317 (-CH₂- twist), 1234 (aromatic C-O str.), 1211 (aliphatic C-N str.), 1059 (aliphatic C-O str.), and 918 (C-H out-of-plane benzoxazine bend.).

Polymerizations of benzoxazines.

Polymerizations were carried out by heating the monomer for one hour at the onset temperature of the respective monomer followed by an additional hour at the temperature of the maximum of exothermic polymerization peak, both temperatures of which were determined by DSC (see characterization). Thus, U-a was heated at 210 and 220 °C, and PH-a was heated at 250 and 260 °C.

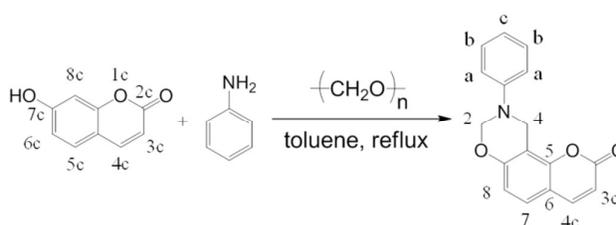
Characterization.

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired on a Varian Oxford AS600 at a proton frequency of 600 MHz. The average number of transients was 64. A relaxation time of 10 s was used for the integrated intensity determination of ¹H NMR spectra. Fourier transform infrared (FTIR) spectra were recorded using a Bomem Michelson MB100 FTIR spectrometer, which was equipped with a deuterated triglycine sulfate (DTGS) detector and a dry air purge unit. Absorption spectra were obtained employing KBr plates, and using 64 scans at a resolution of 4 cm⁻¹. Differential Scanning Calorimetry (DSC) measurements were carried out in a TA Instruments DSC Model 2920 with a nitrogen flow rate of

60 mL/min. Thermograms of the monomers were obtained using a heating rate of 10 °C/min, whereas the glass transition temperature (*T_g*) of the polybenzoxazines were determined employing a sample mass of around 10 mg and a heating rate of 20 °C/min. All samples were sealed in hermetic aluminum pans. Thermal decomposition of the polybenzoxazines was determined by thermogravimetric analysis using a TA Instrument Model Q500 TGA. The TGA analysis was performed in a single heating run from room temperature to 900 °C (ca 2 mg) at a heating rate of 10 °C min⁻¹, with a nitrogen flow rate of 60 mL/min.

Results and discussion

Monomeric benzoxazine resins can in general be straightforwardly synthesized by carrying out different experimental protocols of a modified Mannich reaction.⁵ Regardless of the chosen procedure for the synthesis, benzoxazines with designed chemical structures can be prepared through the proper combination of phenols, amines and formaldehyde for tailored properties. As mentioned in the introduction, the main interest in our molecular design consisted in simultaneously achieving two, apparently opposite, objectives. On the one hand, it was the valorization of natural resources as raw materials for the generation of novel materials. On the other hand, it was the preparation of a resin that can be used to generate thermoset materials with fairly high thermal stability. To achieve this double objective we designed the synthetic pathway presented in **Scheme 1**.



Scheme 1. Synthesis of umbelliferone-aniline benzoxazine resin, U-a, from umbelliferone (7-hydroxy coumarin), aniline, and paraformaldehyde. Pure Roman numerals denote positions in the benzoxazine nuclei, Roman numerals accompanied by the letter c indicate positions in the coumarin portion not overlapped with the benzoxazine, and the pure letters show position in the amine portion of the benzoxazine.

Relatively similar structural motifs in other natural-based compounds (cinnamate-containing benzoxazines)¹² have been reported to have relatively low polymerization temperatures. However, their thermal properties were not desirable, as evidenced by their thermal decomposition temperatures even below their polymerization temperature. To overcome this problem, catalysts were employed to lower even more the polymerization temperature of this cinnamate-containing benzoxazines, thus avoiding this thermal degradation. In this manner, the thermosets were synthesized without significant

degradation. Nevertheless, the resulting polybenzoxazines still exhibited low char yield (lower than 40%). It has been proposed that the breaking of the labile bond between the benzoxazine nuclei and the C=C double bond from the substituent generates a volatile fraction, which not only explains the low char yield obtained but is also assumed to trigger the decomposition. A previously reported coumarin-containing benzoxazine has also been shown to have a relatively low polymerization temperature.¹³ However, once again, the resulting thermoset exhibited poor thermal properties. Although the authors did not explain the reasons for such a behavior, it could be assumed that the presence of aliphatic substituent on the resin may generate volatile fractions, triggering the decomposition and generating low char yields.

Understandably, and depending on the standpoint, particular interest or applications, this **U-a** molecule can be seen at the same time as a coumarin or a benzoxazine derivative. In our study we decided to take it as a benzoxazine derivative. Therefore, the position numbering of **U-a** in this work follows the benzoxazine convention as shown in Scheme 1.

As it can be seen in the previous scheme, compound 7-hydroxy-2H-1-benzopyran-2-one, also referred to as 7-hydroxycoumarin or simply umbelliferone, was chosen as a natural renewable source of phenol for a conventional synthesis of benzoxazine. This simple although smart chemical design allowed us to maintain a C=C double bond as substituent in position 6, which is assumed to lower the polymerization temperature of the benzoxazine. However, this C=C double bond is also linked to a carbonyl group belonging to an ester which is in turn bonded to the benzoxazine nuclei. This architectural motif would avoid the generation of volatile fractions caused by breaking the covalent bond linking the C=C double bond and the benzoxazine. As a result, the triggering of the low temperature degradation is eliminated. Therefore, the thermal properties of the herein designed resin might be enhanced. In comparison to the previously reported coumarin-containing benzoxazine, the content of aliphatic moieties in our designed resin is much lower which might benefit its thermal stability.

The successful formation of the proposed chemical structure for **U-a** is studied by FTIR spectroscopy. **Figure 1** shows the FTIR spectrum of **U-a**. The band present at 1716 cm⁻¹ is attributed to the C=O stretching from the coumarin moiety, whereas characteristic bands, such as 1360, 1211, 1234, 1059, and 918 cm⁻¹ are attributed to the benzoxazine structure, namely, the C-N-C symmetric and asymmetric stretching, C-O-C symmetric and asymmetric stretching, and C-H out-of-plane bending in the aromatic ring fused to the oxazine ring, respectively.

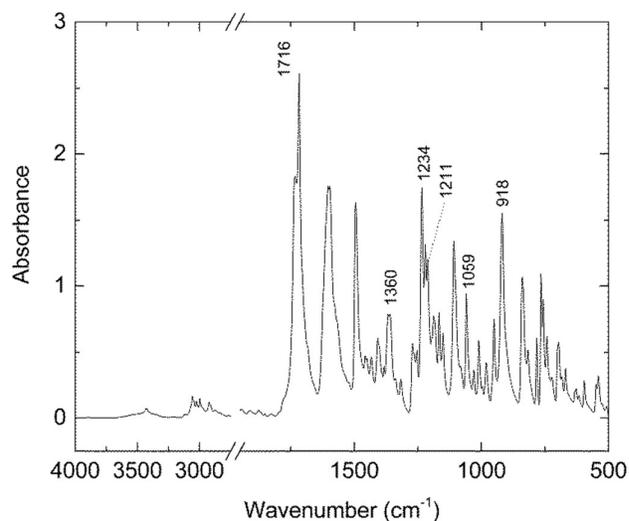


Fig. 1. FTIR spectrum of **U-a**.

Further analysis on the chemical structure of the coumarin-containing resin was obtained by ¹H NMR spectroscopy. **Figure 2** shows the ¹H NMR of **U-a**, where the chemical shifts of the protons of the methylene groups in the oxazine ring, H2 and H4, can be clearly observed at 5.43 and 4.81 ppm, respectively. The two doublets at 7.59 and 6.23 ppm belong to the protons of the conjugated double bond, H4c and H3c, respectively. The 1:1 integration ratio between H7 and H8 complemented with their corresponding multiplicity (doublet) in addition to the absence of a singlet (position 8c occupied, Scheme 1) in the entire aromatic region²⁴ evidences that only one isomer was obtained. This observation is in agreement with the chemical structure depicted in Scheme 1.

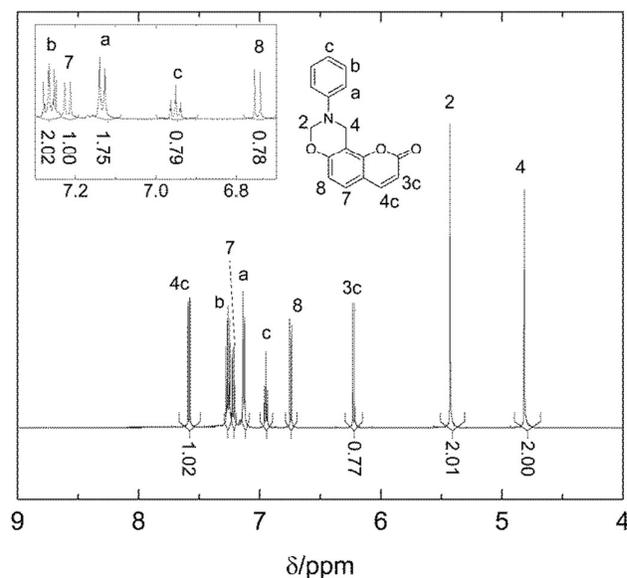


Fig. 2. ¹H NMR spectrum of **U-a**.

The thermal behavior of the synthesized coumarin-containing benzoxazine resin, **U-a**, with respect to its polymerization was studied by DSC and the results are discussed next.

The DSC thermogram of **U-a**, is presented in **Figure 3**. An endothermic process at 147 °C is observed and attributed to the melting of the resin. The DSC thermogram also exhibits a sharp polymerization exotherm maximum at 220 °C, with its onset at 215 °C. Moreover, no decomposition process is observed in the complete range of temperature.

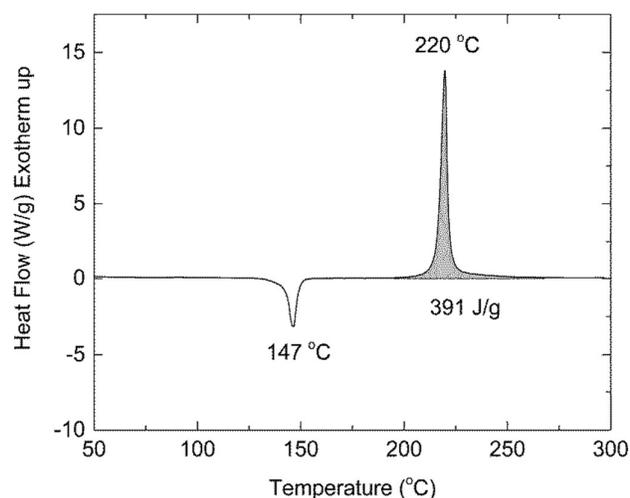


Fig. 3. DSC thermogram of **U-a**.

The sharpness and symmetry of the thermal events observed, especially the endotherm, indicates the high purity of the sample. Thus, influence or catalytic effect produced by impurities affecting the polymerization might be neglected. Furthermore, **U-a** does not bear any catalytic functional group in its chemical structure. Despite these facts, however, **U-a** shows an interesting and unusually low polymerization temperature.

The previous results reinforced our original interest in utilizing natural renewable resources as raw materials for thermoset materials. At the same time, they served as an extra motivation to understand and correlate the chemical structure of this coumarin-containing benzoxazine resins and its corresponding coumarin-containing polybenzoxazine thermoset with their thermal properties. Therefore, the polymerized **U-a**, hereinafter referred to as **poly(U-a)**, was also studied with respect to its thermal properties.

The first step to realize this study on the **poly(U-a)** was to actually polymerize **U-a**. The polymerization condition was based on the DSC results, and performed in four stages as follows: 1) heating at a rate of 10 °C/min until the onset of the polymerization (215 °C); 2) isothermal heating for 1 h at this temperature; 3) heating at the same 10 °C/min rate until the exotherm peak temperature (220 °C); and, 4) 1 h of isothermal heating.

The DSC thermograms of **poly(U-a)** and **poly(PH-a)** presented in **Figure 4** were measured at a heating rate of 20 °C/min. The T_g was calculated as the midpoint of the inflection.

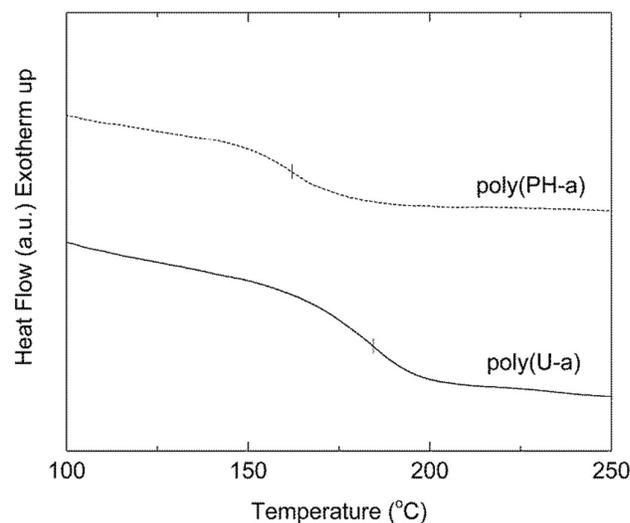


Fig. 4. DSC thermograms of **poly(U-a)** and **poly(PH-a)**.

The DSC thermogram shown in **Figure 4** indicates that **poly(U-a)** has a T_g of 183 °C. It is worth mentioning that no other thermal event other than the T_g is observed in the thermogram within the studied temperature range.

It can be concluded from the DSC results that **U-a** was fully polymerized into **poly(U-a)** since no exothermic peak was detected in the thermogram of the polymerized sample. Moreover, **poly(U-a)** has a higher T_g than the unsubstituted **PH-a**, which are 183 °C and 162 °C, respectively. This result is similar to those reported for cinnamate-containing¹² and aliphatic ester-containing benzoxazines.²⁵ Furthermore, this T_g value of **poly(U-a)** is comparable to extensively studied bisphenol A and aniline-based benzoxazine, **BA-a**. Based on the chemical structure of the coumarin-containing benzoxazine resin, this result was not unexpected. This may be explained by considering that two of the free and usually active positions for polymerization and cross-linking reactions in the aromatic ring, adjacent to the oxazine moiety, are occupied in **U-a** bearing the coumarin moiety. This would reduce the number of cross-linking sites in the benzoxazine nuclei, thus reducing consequently the T_g of the coumarin-containing resin. This rationalization is consistent with results and explanations for the T_g values of cinnamate-containing benzoxazines,¹² especially for a methyl ferulate which bears two substituents in the aromatic ring adjacent to the oxazine ring. Nevertheless, it is rather surprising to see that **poly(U-a)** exhibits good thermal stability.

TGA measurements were carried out to gain further insights on this unusual stability of **poly(U-a)**. The TGA thermogram is shown in **Figure 5**. Then, to perform an actual evaluation of

the stability of this polybenzoxazine, the main thermal properties, T_{d5} and T_{d10} , defined as the temperatures at which the weight loss is 5 and 10% respectively, as well as the char yield, defined as the residual weight at 800 °C measured under N_2 atmosphere, were measured.

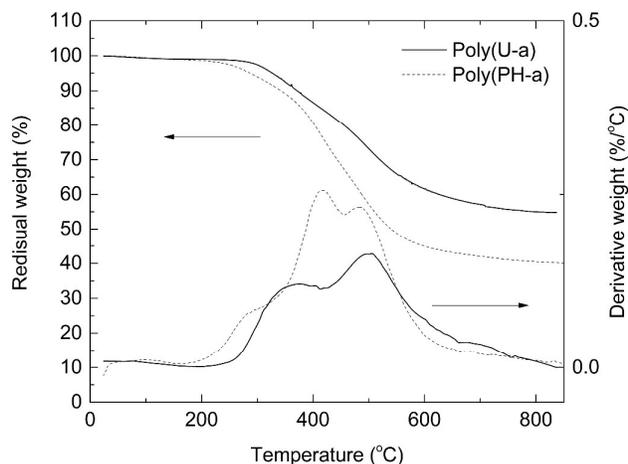


Fig. 5. TGA thermograms of **poly(U-a)** and **poly(PH-a)**.

In general, polybenzoxazine degradation shows a three steps process.²⁶ Thus, it can be seen in Figure 5 a minor weight loss between room temperature and 300 °C, followed by a pronounced weight loss between 300 and 560 °C, and lastly a small gradual degradation from 560 to 800 °C. More quantitative information obtained from the TGA measurement is presented by the following values, T_{d5} of 327 °C, T_{d10} of 373 °C, and specially a char yield as high as 55%. Once again, although this time by TGA, a good thermal stability of **poly(U-a)** is observed.

In general, a high char yield accompanied of a broad degradation profile at high temperatures with a slow decomposition rate are the favorable characteristics for a polymer to be considered as a good anti-flammable material.^{14, 27} Thus, based on the previous results, one could envision **poly(U-a)** or related thermoset materials as promising and interesting candidates for this application.

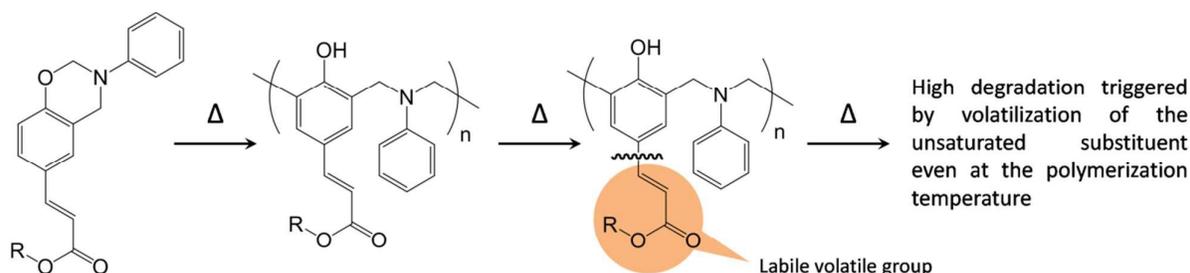
The results herein presented are of particular relevance since, to the best of our knowledge, this novel coumarin-containing polybenzoxazine based thermoset material is shown to possess better thermal properties than any other similar structures¹³ or comparable benzoxazine resins from natural renewable resources reported to date.^{12, 14} For instance, a different coumarin-containing benzoxazine has been shown to start degrading below 280 °C and generating a char yield of only 36%.¹³ Alternatively, thermal studies have demonstrated that a family of cinnamic and cinnamate-containing benzoxazines shows degradation even at the polymerization temperature and their polymers generate char yields between 30 to 40%.¹² A fragmentation of the unsaturated substituent

belonging to the cinnamic/cinnamate portion and the subsequent volatilization of the generated small fraction has been reported as the first event in the degradation of this kind of polybenzoxazines. This decomposition occurs at relatively low temperatures (130-200 °C) because the covalent bond linking the unsaturated substituent to the aromatic ring is labile. Although no further details have been reported about the mechanism of the degradation, this initial fragmentation is assumed to act as the trigger for the subsequent full degradation of the polybenzoxazine.¹² The process is depicted in **Scheme 2.a**.

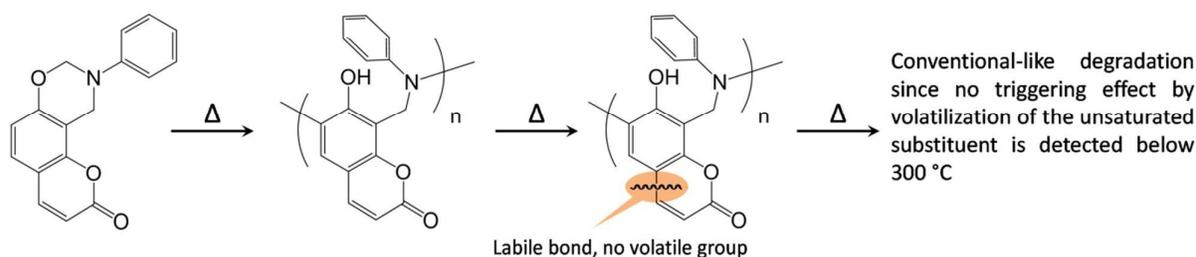
As shown in Scheme 2.b., the herein presented **poly(U-a)** bears a similar labile covalent bond between the aromatic ring from the polybenzoxazine and the carbon from the C=C double bond. In a simple interpretation, the coumarin-containing benzoxazine can actually be seen as a conventional benzoxazine substituted in position 5 and 6. The substituent groups would then be an $-OC(O)R$ in position 5 and an activated olefin in position 6. Thus, these “two substitutions” may affect its polymerization as well as the thermal stability in the resulting thermoset. While polymerization aspects will be reported elsewhere, rationalization of the thermal stability is discussed next. A deep look at the chemical structure of **U-a** and **poly(U-a)** shows that the two substituents are indeed linked to each other thus forming the coumarin moiety. An important consequence of this internal connectivity is that no volatile fraction is generated after breaking the labile bond linking the aromatic ring from **poly(U-a)** to the activated olefin. Thus, the event assumed to trigger the decomposition on the cinnamic/cinnamate-containing polybenzoxazines is not occurring in the coumarin-containing thermoset. Thus, low temperature decomposition is not an issue in our novel designed coumarin-containing polybenzoxazine thermoset. This easily explains the good thermal stability of **poly(U-a)**.

It is worth emphasizing that thermal stability could be seen or interpreted differently depending on the particular application the material is designed for. For example, a vanillin-containing polybenzoxazine (**poly(V-a)**) has been reported¹⁴ to start its degradation process at about 280 °C, which would suggest lower thermal stability than the herein presented **poly(U-a)**. Nevertheless, this same **poly(V-a)** also presented a char yield of 55%, which may indicate higher thermal stability than **poly(U-a)**. This last result might be the consequence of additional or side reaction during the polymerization. For instance, the aldehyde group present in this vanillin-containing benzoxazine resin was reported to participate in the conventional benzoxazine polymerization mechanism.^{28, 29} This fact may not only affect the polymerization itself but also the properties of the final material.

a) Cinnamic/cinnamate-containing benzoxazine and polybenzoxazine

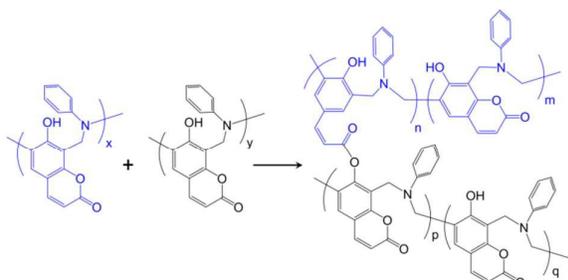


b) Coumarin-containing benzoxazine and polybenzoxazine



Scheme 2. a) Polymerization of cinnamic/cinnamate-containing benzoxazines and their possible degradations triggered by the generation of small volatile fragments by breaking the bond linking the polybenzoxazine moiety and the C=C double bond. Adapted with permission.¹² Copyright 2013, Wiley. b) Polymerization of **U-a**. No generation of volatile fragments are detected even if the bond linking the polybenzoxazine moiety and the C=C double bond might be broken.

In this regard, the relatively high char yield (55%) obtained for **poly(U-a)** may be explained not only by the lack of formation of volatile fragments at low temperatures, but also by possible additional cross-linking reaction as the reported transesterification between ester groups present in the benzoxazine resins and the -OH generated during polymerization of the benzoxazines.^{12, 25} A schematic representation of this kind of transesterification is depicted in **Scheme 3**.



Scheme 3. Proposed transesterification reaction responsible to increase the natural cross-linking in polybenzoxazines.

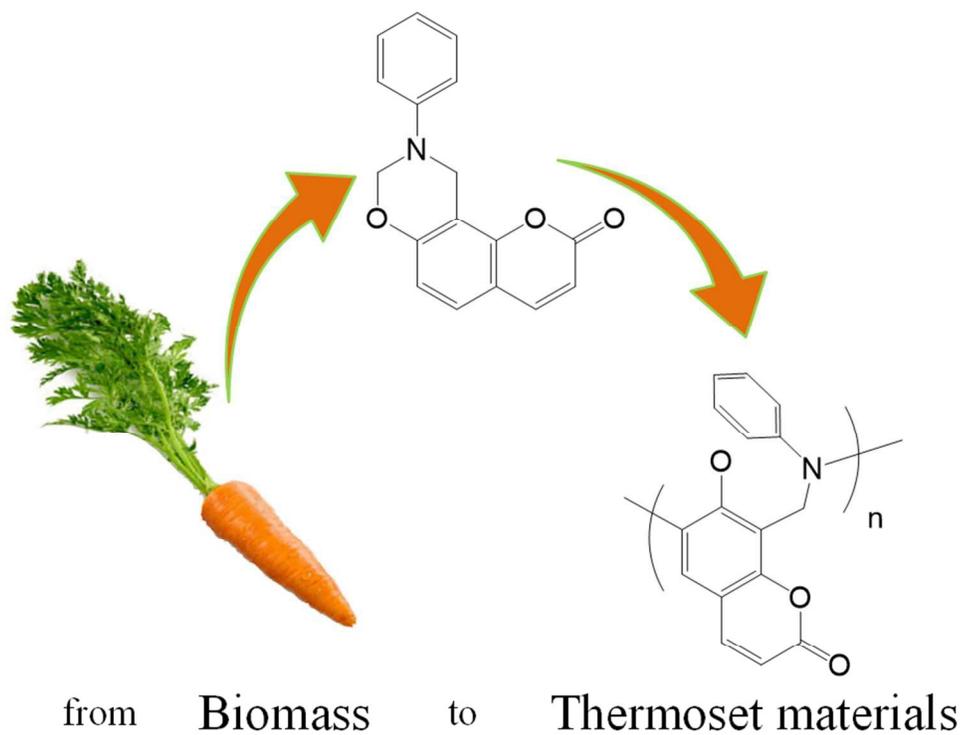
Conclusions

A novel coumarin-containing benzoxazine resin, **U-a**, was successfully designed and synthesized using umbelliferone (7-hydroxy coumarin) as a natural renewable phenol source. This biomass-based benzoxazine resin showed to be easily and fully polymerizable showing no degradation at the polymerization temperature. Thus, the use of catalysts during polymerization is not required. The resulting thermoset material, **poly(U-a)**, exhibited good thermal properties as demonstrated by its high char yield (>55%) and relatively high degradation temperature (>300 °C). Therefore, this natural renewable resource coumarin-based benzoxazine resin herein reported is shown to be comparable to their petroleum-based analogs toward the design, synthesis and applicability of thermoset materials.

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