Tailor-Made and Chemically Designed Synthesis of Coumarin-Containing Benzoxazines and Their Reactivity Study Toward Their Thermosets

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Received 7 October 2015; accepted 11 November 2015; published online 17 December 2015
DOI: 10.1002/pola.27994

ABSTRACT: Coumarins are used as a natural renewable resource to synthesize coumarin-containing benzoxazine resins. The coumarin-containing benzoxazines are fully characterized in terms of their chemical structure by Fourier-transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy. The influence of electronic effects caused by the substituents on the polymerization temperature is also evaluated. Thermal properties of the resulting thermosets are characterized by differential scanning calorimetry and thermogravimetric analysis, showing good stability and char yields higher than 50%. The coumarin-containing polybenzoxazine thermosets show T_g values in the range between 160 and 190 °C. Thus, the herein presented coumarin-containing benzoxazine resins are proven to be competitive monomers when compared with other petroleum-based benzoxazine resins toward the generation of high-performance thermoset. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1428–1435

KEYWORDS: chemical design; polybenzoxazines; renewable resources; sustainable chemistry; thermosets

INTRODUCTION Polybenzoxazine is a relatively new class of thermoset material attracting researchers' attention from both scientific and industrial communities. For instance, while much work and effort are still being invested in further developing deeper understanding and new formulations for this kind of polymers, benzoxazines and polybenzoxazines are already commercially available. Polybenzoxazines are synthesized by cationic ring-opening polymerization of 1,3-benzoxazine resins.[1] As in other polymers, the properties exhibited by polybenzoxazines strongly depend on the nature of the benzoxazine monomer and the manner, in which the polymerization is carried out. Polybenzoxazines can be polymerized without added initiator or catalyst requiring in general temperatures in the range of 150–230 °C, although some benzoxazines have been shown to polymerize at lower temperature.[2] Thus, the use of catalysts aiming at reducing the polymerization temperature has also been investigated.[3–5] However, these complex systems in which additional compounds must be added might not be fully beneficial from an economic nor practical standpoint since extra effort must be put on the processing and this could also affect the very desirable properties of the final product.[6,7] On the contrary, it would certainly be advantageous if the monomeric benzoxazines themselves could be tailor-made and chemically designed in such a manner to be able to polymerize at exact programed temperatures with high precision without affecting the final properties of the polybenzoxazines.

It would be also beneficial if new industrial polymeric systems can be prepared from natural renewable materials.[8–10] As known, the synthesis of benzoxazines involves phenolic compounds. They are usually derived from the petrochemistry but could easily be replaced by other biomass-based phenolic compounds.[11–14] The feasibility of using biomass renewable resources as raw materials for the synthesis of benzoxazine resins has been reported[15] by not only substituting the phenolic moiety but also the amine portion[16] of the resins. Expectedly, attempts were also made to replace both the phenolic and the amine moieties,[17] placing the benzoxazines as pending groups in existing natural occurring polymers,[18] and copolymerizing benzoxazines with natural renewable oligomers.[19]

In this regard, coumarins can be considered as a viable alternative for the synthesis of benzoxazines[12] since they are in general natural and renewable compounds in themselves, or they can be directly obtained from other derivatives from the biomass such as resorcinol.[20] Of particular interest are coumarins bearing a hydroxyl group in position 7, such as umbelliferone and 4-methylumbelliferone. These two compounds

present their *ortho* positions unsubstituted with respect to the hydroxyl group, thus making them good phenolic reactants toward the synthesis of 1,3-benzoxazines. Additionally, if the focus is addressed to the benzoxazine nuclei the coumarin moiety (e.g., umbelliferone) could be viewed as a substituent, which will provide specific properties and reactivity to the resulting benzoxazine. Then, substituted coumarin moieties (for instance, 4-methylumbelliferone) should in consequence be viewed as substituted substituents, which will modify the specific properties and reactivity of the benzoxazine. Knowing the features of each moiety forming the entire molecule, one may be able to understand its behavior. Nevertheless, the knowledge might be used to chemically design compounds with tailored properties and reactivity.

Having this motivation, the present work aims to uncover the contribution of each substituent on coumarin-based benzoxazines and correlate them to the thermal properties. This article supplements our earlier report on the synthesis and characterization of a coumarin-functional benzoxazine monomer and its cross-linked material.[21]

EXPERIMENTAL

Material

Aniline, 4-methylumbelliferone (≥98%), and paraformaldehyde (96%) were used as received from Sigma-Aldrich. Umbelliferone (>98%) was purchased from TCI America. 3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine (**PH-a**) was synthesized and purified following a procedure described elsewhere.[22] Toluene and basic alumina were purchased from Fischer scientific and used as received.

Synthesis of Coumarin-Containing Benzoxazines

General procedure:

Aniline (15 mmol), 4-methylumbelliferone (15 mmol), paraformaldehyde (33 mmol), and toluene (20 mL) were placed into a 50 mL round-bottomed flask equipped with magnetic stirring and refluxed for 12 h. The crude product was diluted with toluene (25 mL) and passed through a basic alumina column. After solvent removal, the resulting yellow–white crystals were purified by recrystallizing in toluene at low temperatures.

9-phenyl-9,10-dihydro-2H,8H-Chromeno[8,7-E][1,3]oxazin-2-One (U-a)

U-a was obtained with a yield of 65%. ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C) δ, ppm: 7.59 (d, 1H, Ar-C*H*═CHR (HIV)), 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═C*H*-COOR (HIII)), 5.43 (s, 2H, Ar-O-CH_2-NR (H_2)), and 4.81 (s, 2H, Ar-CH_2-NR (H4)). FT-IR ν (cm^{-1}): 1716 (C═O str.), 1433 (CH_2 sciss.), 1360 (aromatic C–N str.), 1317 (–CH_2– 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.). All spectral details are reported in Ref. [21].

4-methyl-9-phenyl-9,10-dihydro-2H,8H-Chromeno[8,7-E][1,3]oxazin-2-One (MU-a)

MU-a was obtained with a yield of 70%. ^{1}H NMR (600 MHz, CDCl3, 20 °C) δ, ppm: 7.35 (d, 1H, H_7), 7.25 (d, 2H, H_b), 7.12 (d, 2H, H_a), 6.94 (t, 1H, H_c), 6.76 (d, 1H, H_8), 6.11 (s, 1H, -C(CH_3)═C*H*-COO-), 5.42 (s, 2H, –O-CH_2-N–), 4.81 (s, 2H, Ar-CH_2-N-), and 2.36 (2, 3H, Ar-C(CH_3)═CH-). FT-IR ν (cm^{-1}): 1732 (C═O str.), 1433 (CH_2 sciss.), 1356 (aromatic C–N str.), 1313 (–CH_2– twist), 1265 (aromatic C–O str.), 1215 (aliphatic C–N str.), 1057 (aliphatic C–O str.), and 908 (C–H out-of-plane benzoxazine bend.).

Preparation of the Polybenzoxazines

Polymerizations were carried out by heating at a rate of 10 °C/min until the onset of the polymerization temperature for each monomer, followed by isothermal heating for 1 h at this temperature. Next, samples were heated at the same 10 °C/min rate until the exotherm peak temperature, followed by 1 h of isothermal heating. Both onset and exotherm peak temperature in each system were obtained from DSC experiments. Thus, **U-a** was heated at 210 and 220 °C, **MU-a** at 220 and 232 °C, while **P-a** at 250 and 260 °C.

Characterization

Proton nuclear magnetic resonance (^{1}H 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 ^{1}H NMR spectra. Fourier transform infrared (FT-IR) spectra were recorded using a Bomem Michelson MB100 FT-IR 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 was 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. TGA analysis was performed in a single heating run from room temperature to 900 °C (*ca* 3 mg) at a heating rate of 10 °C/min, with a nitrogen flow rate of 60 mL/min. All thermal analysis and polymerizations were carried out under nitrogen atmosphere.

RESULTS AND DISCUSSION

As described in the Introduction section, the interest of this work was on designing coumarin-containing benzoxazines with programmable polymerization temperatures. It is then helpful to first identify not only each component nuclei, benzoxazine, and coumarin, but also every position on the resulting coumarin-based benzoxazine molecule. Figure 1 shows the numbering on each individual class of molecule

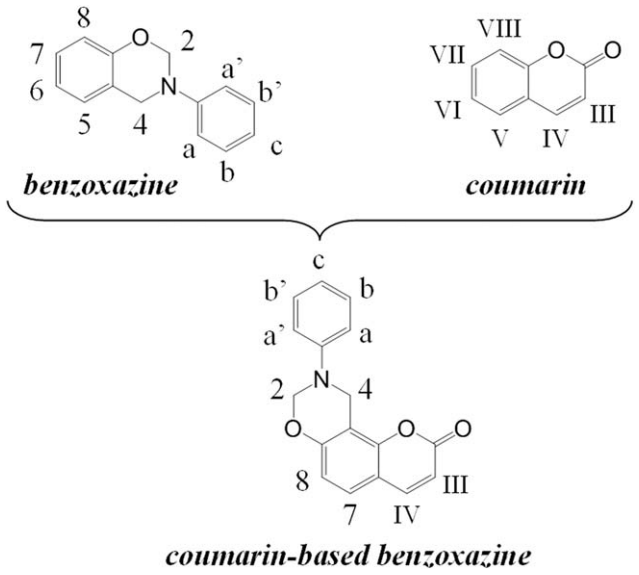


FIGURE 1 Full numbering in benzoxazine and coumarin nuclei showing complete identification of each position in each class of molecule individually. Briefly, Arabic numbers are used in the benzoxazine nuclei and Latin letters are used in the aniline portion. Roman numbers describe the different position in the coumarin nuclei. An apostrophe (') is used to show that two positions apparently chemically and/or magnetically equivalent could, in fact, be different.

nuclei, benzoxazine, and coumarin, as well the resulting coumarin-containing benzoxazines. It can be seen in the figure that the conventional numbering system in each nuclei is respected, using Arabic numbers on the benzoxazine nuclei and Roman ones on the coumarin. To avoid confusions, in the resulting coumarin-containing benzoxazines, each number system is respected.

Using two different coumarins bearing one functionalizable hydroxyl group, such as umbelliferone and 4-methylumbelliferone, it is possible to design and synthesize two different coumarin-based benzoxazines. Thus, Scheme 1 shows how umbelliferone-aniline benzoxazine (**U-a**) and 4-methylumbelliferone-aniline benzoxazine (**MU-a**) were successfully prepared *via* the Mannich condensation reaction using aniline as the amine, umbelliferone, and 4-methylumbelliferone as the phenol source and paraformaldehyde in refluxing toluene.

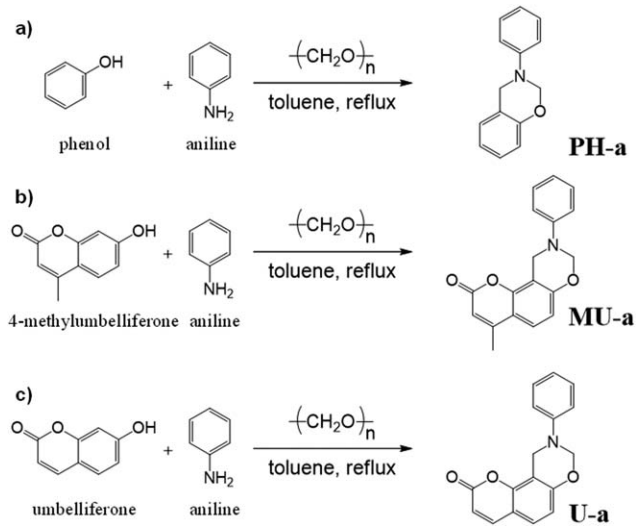
Formation of the structures of **MU-a** was studied by FT-IR spectroscopy (Fig. 2). The spectrum shows expected similarities to other coumarin-containing benzoxazines, except for the particular methyl group present in position IV. Thus, a C═O stretching bands is observed at 1732 cm^{-1} for **MU-a**. The shift of this C═O stretch band to a higher frequency compared to the one from **U-a** (observed at 1716 cm^{-1}, see Experimental section) is due to the methyl group of **MU-a** since forces the carbonyl group to be slightly out of plane, thus interfering with the resonance. Typical benzoxazine's C–N–C symmetric and asymmetric stretching are observed at 1356 and 1215 cm^{-1}. Similarly, the C–O–C symmetric and asymmetric stretching bands are found at 1265 and 1057 cm^{-1}. Finally, the characteristic band assigned to C–H out-of-plane bending in the aromatic ring fused to the oxazine ring is observed at 908 cm^{-1}. These results indicate the coexistence of the two nuclei, benzoxazine and coumarin, which suggest the success synthesis of **MU-a**.

The chemical structure of **MU-a** was further studied and confirmed by ^{1}H NMR spectroscopy. Figure 3 shows the ^{1}H NMR spectrum. As in FT-IR analysis, chemical shift values of each signal generated by protons belonging to **MU-a** show high similarities to other coumarin-based benzoxazines given the nature of their chemical structures. Thus, the characteristic resonances belonging to the methylene groups in the oxazine ring are found at 5.42 and 4.81 ppm in the spectrum of **MU-a**. Unlike **U-a**, which bears one proton in position III and one in position IV observed as doublets at 6.23 and 7.59 ppm (see Experimental section), **MU-a** contains a single proton in position III observed as a singlet at 6.11 ppm and a methyl group at position IV observed as a singlet at 2.36 ppm. As in other reported coumarins substituted in position VII,[23] the absence of a singlet in the entire aromatic region on the spectrum of **MU-a** indicates that only one isomer shown in Scheme 1 and Figure 3 was obtained following the synthesis procedure herein described.

Polymerization behavior of both coumarin-containing benzoxazine resins and the unsubstituted **PH-a** as well as the thermal properties of their corresponding thermosets were investigated by DSC and TGA and are discussed next.

Figure 4 shows the DSC thermograms for the three monomers and a summary of the thermal properties is presented in Table 1.

It can be seen from Figure 4 that each of the three thermograms corresponding to each monomeric resins presented



SCHEME 1 Synthesis of phenol-aniline (**PH-a**), 4-methylumbelliferone-aniline (**MU-a**), and umbelliferone-aniline (**U-a**) benzoxazine resins from phenol, 4-methylumbelliferone, umbelliferone, aniline, and paraformaldehyde.

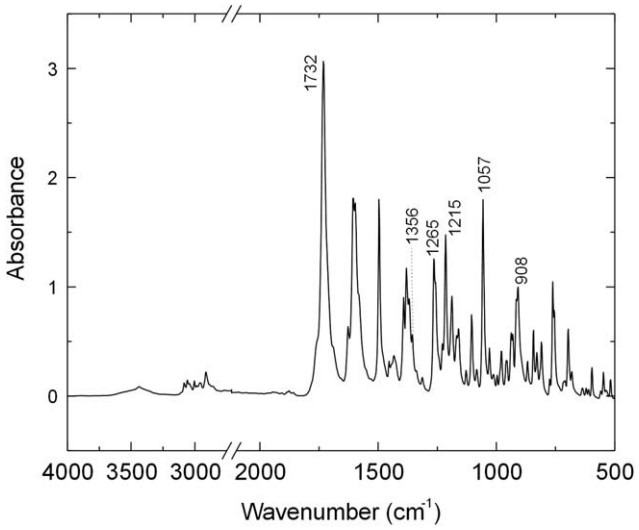


FIGURE 2 FT-IR spectrum of 4-methylumbelliferone-aniline benzoxazine resin (**MU-a**).

two thermal processes clearly defined, an endothermic peak attributed to the melting processes of the resin as well as an exothermic one assigned to their polymerizations.

The benzoxazine resins exhibited melting temperatures of 54 °C for **PH-a**, 147 °C for **U-a**, and 153 °C for **MU-a**, while their polymerization temperatures presented the following pattern: **PH-a** polymerizes at the highest temperature (261 °C), followed by **MU-a** (232 °C), and **U-a** at the lowest temperature (220 °C).

The polymerization temperature pattern can be rationalized straightforwardly by doing structure–property analysis. Compared to the unsubstituted **PH-a**, benzoxazines with the coumarin substituent have significantly reduced the polymerization temperature. Motivated by this fact, we have developed an interest in understanding and correlating the influence of electronic effects on the reactivity of these benzoxazine resins. To achieve this goal, we will first interpret the influence of these electronic effects induced by the substituents on the polymerization mechanism by considering each substituent separately. Next, the manner in which each effect may affect the others will also be taken into account. And finally, the thermal behavior of the entire molecule will be interpreted. To begin, a description of the unique structural parameters of each monomer is presented as follows:

- **PH-a** is considered as reference since no substituents are present in this resin.
- **U-a** is substituted in position 6 (*para* position with respect to the oxygen in the oxazine ring) with a strong electron-withdrawing conjugated C═C double bond, and in position 5 (*meta* position) with the oxygen from the ester group which is a moderately electron-donating group.
- **MU-a** is substituted in position 6 (*para* position with respect to the oxygen in the oxazine ring) with a relatively strong electron-withdrawing conjugated C═C double bond. This double bond is substituted with a weak electron-donating methyl group in its very activated position IV, and also substituted in position 5 (*meta* position) with the oxygen from the ester group which is a moderately electron-donating group.
- When comparing **U-a** with **MU-a** in terms of electronic contribution, the effects generated by the oxygen in position 5 can be overlooked since it should be comparable for both compounds.
- C═C double bond substituents are usually very weak electron-donating groups, whereas activated C═C double bond *via* conjugation such as Michael acceptors behaves as strong electron-withdrawing groups.

As shown in Figure 4, **U-a** is the most reactive resin since it has the lowest polymerization temperature followed by **MU-a**, and finally **PH-a** which has the highest polymerization temperature thus being the least reactive resin. Compound **PH-a** is known to have the four positions in the aromatic ring only slightly activated, being position 8 the most reactive one since it is in the *ortho* position to its most activating group, the oxygen in the oxazine ring.

A straightforward comparison between **PH-a** and both coumarin-containing resins reveals that, in **U-a** and **MU-a**, positions 5 and 6 are occupied by the coumarin moiety, while positions 7 and 8 are unsubstituted. Interestingly, position 8 in the coumarin-containing resins is being simultaneously activated by the oxygen atom in the oxazine ring and the –OC(O)R group, while deactivated by the conjugated C═C double bond which still directs any reaction to position 8. Thus, it is reasonable to accept that both coumarin-containing resins are more reactive than **PH-a** toward the polymerization reaction. By comparing **U-a** to **MU-a**, it can

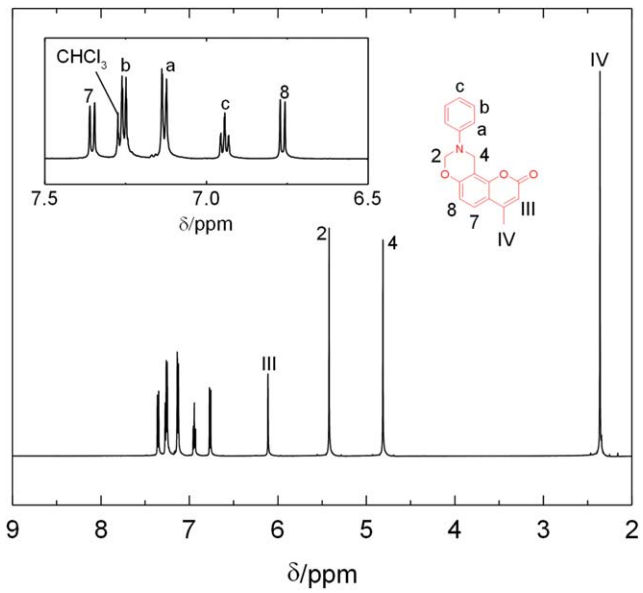


FIGURE 3 ^{1}H NMR spectra of 4-methylumbelliferone-aniline benzoxazine resins (**MU-a**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

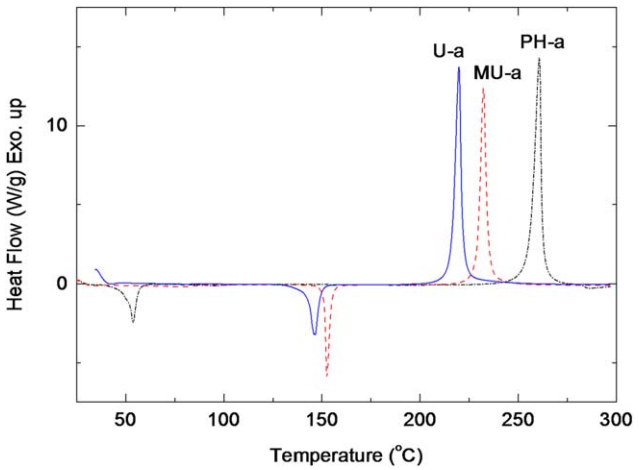


FIGURE 4 DSC thermograms of the benzoxazine resins studied: **PH-a** (-.-), **MU-a** (–), and **U-a** (-). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be seen that they have a similar activation pattern produced by the coumarin moiety over the benzoxazine nuclei, being the methyl group in position IV the only difference. To better understand the influence of this methyl group, and therefore, the difference in reactivity between **U-a** and **MU-a**, localized electronic effects must be considered and explained separately first and then combined together.

As previously mentioned, the C═C double bond from the coumarin moiety can be considered as a single substituent in position 6 in the benzoxazine nuclei. However, this C═C double bond is not isolated in the structure, but instead is conjugated with the carbonyl group of the ester. When a C═C double bond is conjugated with very strong electron-withdrawing groups, such as esters, this double bond becomes part of a more complex system, known as an activated electrophilic olefin, also referred to as a Michael acceptor. Figure 5 depicts an example for the selective activation of this kind of system, where two chemical structures of the same compound are in resonance. This is in fact the reason for this C═C double bond to be considered as a strong electron-withdrawing group substituent in the coumarin-containing benzoxazine resins.[24]

The system in resonance on the right-hand side is less electrophilic than the one at the left due to the weakening effect of the positive charge by the neighboring electron-donating

TABLE 1 Thermal Properties of Benzoxazine Resins

Monomer	Melting temperature (°C)	Polymerization temperature (°C) Onset	Max.
PH-a	54	255	261
U-a	147	215	220
MU-a	153	229	232

methyl group. Clearly, this methyl group is not a direct substituent on the benzoxazine nuclei, and even so it still influences its reactivity. Nevertheless, its effect can straightforward be understood when one considers this methyl group as a substituent of the activated electrophilic olefins which is the actual substituent on the benzoxazine nuclei. Certainly, different activated electrophilic olefins will affect the reactivity of the benzoxazine resins in different manners. This is in fact the case in our systems. Therefore, the two coumarin-containing benzoxazines can be viewed as the same resin bearing two different substituents in position 6. The electrophilicity of this isolated model system is here straightforwardly related to the capacity to act as an electron-withdrawing group when the same motif is a substituent group. Thus, it can be inferred that the substituent in position 6 in **U-a** is a stronger electron-withdrawing group than the one present in **MU-a** at the same position. This results in **U-a** being more reactive than **MU-a** with respect to their polymerization reactions.

Finally, the unsubstituted **PH-a** is the least reactive of all three resins since this benzoxazine is not activated by any means. An idealized polymerization mechanism is proposed for **MU-a** and **U-a**, showing the electronic influence in each monomer (Scheme 2). The classic cationic polymerization of **PH-a** is also presented for comparison.

With the interest of studying the coumarin-containing polybenzoxazines toward potential applications and based on the DSC results, each coumarin-containing resin was polymerized according to the following cycle, tailored for each resin. Each resin was heated at a rate of 10 °C/min until the onset of the polymerization, followed by isothermal heating for 1 h at this temperature. Then, the sample was heated at the same 10 °C/min rate until the exotherm peak temperature, followed by 1 h of isothermal heating. DSC and TGA analyses were carried out on the three polybenzoxazines.

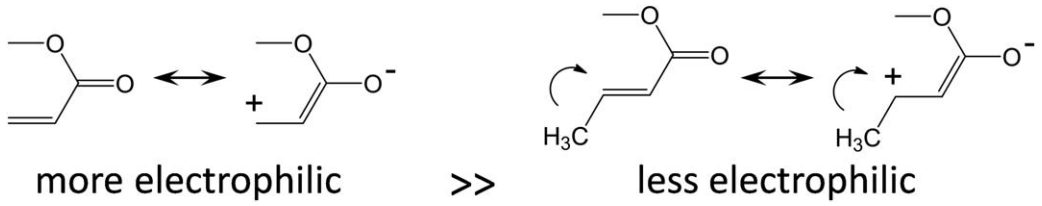
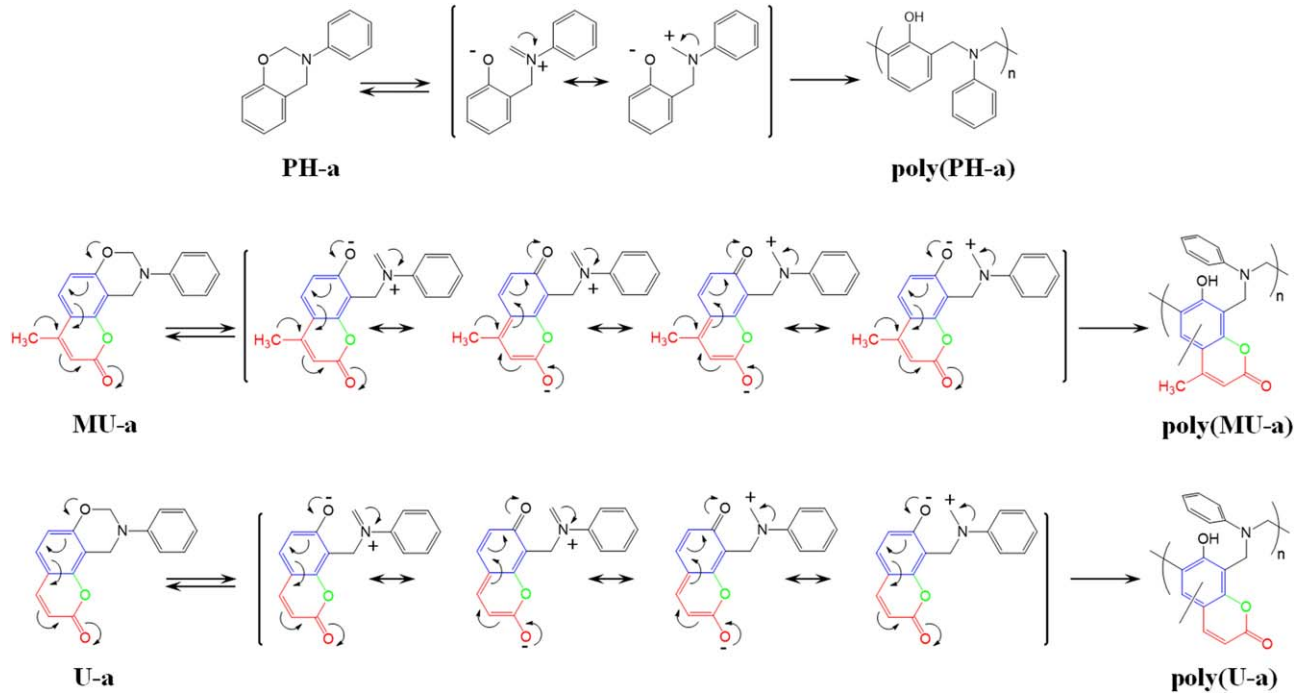


FIGURE 5 Schematic depiction showing the resonance of a compound and the electronic implications, evidencing the origin of the activated electrophilic olefins, also referred to as Michael acceptors.



SCHEME 2 Idealized proposed polymerization mechanism of **PH-a**, **MU-a**, and **U-a** showing the electronic influence in each monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 shows the DSC thermograms of the three polybenzoxazines, **poly(PH-a)**, **poly(MU-a)**, and **poly(U-a)**, which were obtained from the monomeric resins, **PH-a**, **MU-a**, and **U-a**, respectively.

The DSC thermograms indicate that **poly(MU-a)** has a T_g of 189 °C which is the highest, followed by **poly(U-a)** at 183 °C, while **poly(PH-a)** exhibits the lowest one at 163 °C.

The relatively low T_g values for these coumarin-containing polybenzoxazines were in a way expected. A reason for this can be rationalized by the fact that two of the usually active positions for polymerization and cross-linking reactions in the aromatic ring, adjacent to the oxazine moiety, are occupied by the coumarin moiety. These results might suggest that **poly(MU-a)** is the most cross-linked of the three polybenzoxazines obtained after polymerization, followed by **poly(U-a)** and finally **poly(PH-a)** which is the least cross-linked. However, another reason for the higher T_g of **poly(MU-a)** compared to that of **poly(U-a)** might be due to the presence of the methyl group in the repeating units, which increases the steric constraints toward molecular rearrangement and consequently impairing chain mobility resulting in a higher value of T_g. **Poly(PH-a)** shows the lowest value of the T_g obtained in this study and is consistent with results previously reported in the literature.[11] It has been documented that a higher cross-linking in methyl cinnamate-containing resins, with respect to the unsubstituted **PH-a**, is due to additional cross-linking sites, such as the extra C=C double bond, as well as more possible cross-linking reactions as the reported transesterification between ester groups and the –OH generated during polymerization of the benzoxazines.[11,21,25]

The second result observed in Figure 6 for these fully polymerized polybenzoxazines is that all three systems showed to be very stable in the entire range of temperatures analyzed since no degradation process was detected. This result is of particular importance since the two coumarin-containing polybenzoxazines herein presented are more stable than any other similar or comparable systems derived from natural renewable resources found in the literature.[11,12]

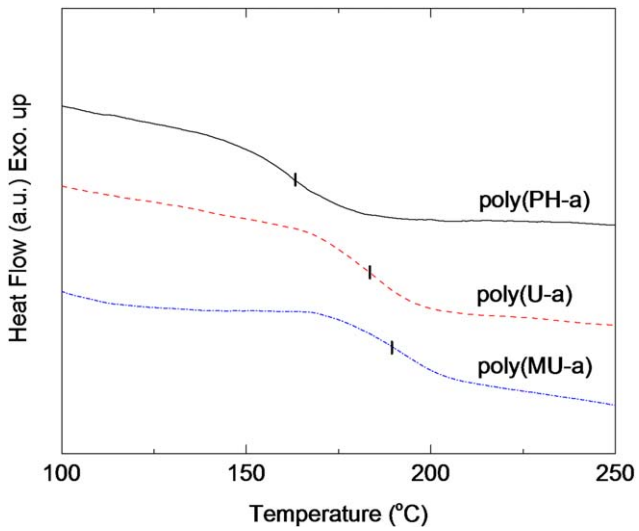


FIGURE 6 DSC thermograms of **poly(PH-a)**, **poly(MU-a)**, and **poly(U-a)**. T_g was defined as the midpoint of the inflection. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

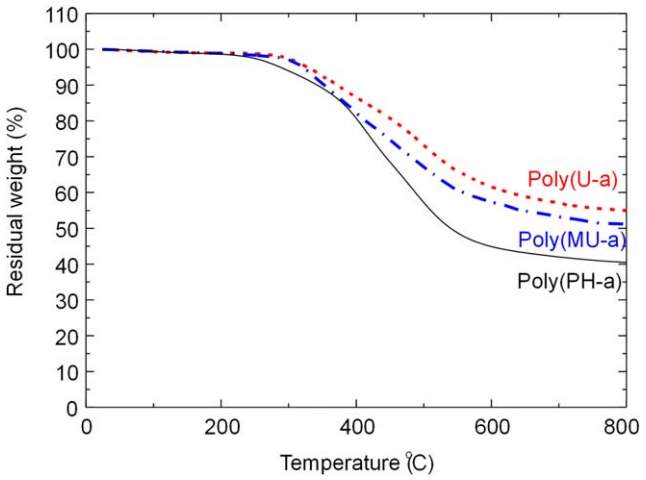


FIGURE 7 TGA thermograms of the coumarin-containing polybenzoxazines: **poly(U-a)**, **poly(MU-a)**, and **PH-a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal degradation of conventional polybenzoxazines has been reported to proceed following mainly three steps: (a) evaporation of the amine from the chain ends and branches; (b) evaporation of the amine from the main chain; and (c) the simultaneous breakage of the phenolic linkage and degradation of the Mannich base.[26] The specific temperatures at which these general features may occur and the profile of the thermogram could certainly be altered depending on different possible chemical structures, degree of cross-linking as well as quantity and nature of existing substituent groups. For instance, while one coumarin-containing benzoxazine has been reported to start its degradation at temperatures around 275 °C generating a char yield of only 36%,[12] a novel coumarin-based benzoxazine was recently chemically designed to be thermally more stable, starting its degradation at higher temperature and generating a char yield of 55%.[21]

To further investigate the unexpected stability of the cross-linked coumarin-containing polybenzoxazines herein presented, TGA measurements were carried out and the results are shown in Figure 7. A summary of the main thermal properties, T_{d5} and T_{d10}, defined as the temperatures at which the weight loss is 5% and 10% respectively, and the char yield, defined as the residual weight at 800 °C under N_2 atmosphere, are presented in Table 2.

TABLE 2 Thermal Properties of Benzoxazine Resins

Thermoset	T_g (°C)	T_{d5} (°C)[a]	T_{d10} (°C)[b]	Char yield (%)[c]
Poly(U-a)	183	320	353	55
Poly(MU-a)	189	312	361	51
Poly(PH-a)	163	288	343	40

[a] Temperature at which the weight loss is 5%.
[b] Temperature at which the weight loss is 10%.
[c] Char yield, defined as the remaining weight% at 800 °C, measured under N_2.

Figure 7 shows the monotonous degradation profiles for both polybenzoxazines, **poly(U-a)** and **poly(MU-a)**. Both thermosets underwent very little weight loss below 310 °C, showing their high thermal stability. The main degradation occurred from 310 to 560 °C, where the main weight loss is observed in the thermograms. A slow degradation profile takes place from there to 800 °C, where the high char yield obtained for each polybenzoxazine evidenced once again the high thermal stability. As previously discussed for the DSC results, and once again demonstrated by the relatively high T_{d5}, T_{d10}, and specially the high char yields generated by our coumarin-containing polybenzoxazines (**poly(U-a)** and **poly(MU-a)**), a good thermal stability has been achieved for **poly(MU-a)** without significantly affecting the polymerization temperature when compared to **poly(U-a)**. This is of special importance because it shows that these two different thermosets with similar properties can be designed and synthesized using different compounds obtained from different natural renewable resources. Additionally, and to the best of our knowledge, these materials exhibit better thermal properties than any other similar structures[11,12] and comparable benzoxazine resins from natural renewable resources reported to date.[27] The additional advantage of knowing and understanding the chemistry behind the process let us manipulate by design the systems to obtain different materials exhibiting similar desirable properties.

CONCLUSIONS

Novel coumarin-containing benzoxazine resins were successfully synthesized using coumarins as phenolic raw materials, which are a family of natural renewable resources. The implications of the electronic effects caused not only by the coumarin itself on the reactivity of benzoxazine toward polymerization, but also the one induced by the methyl group modifying the coumarin, which in turn ended to affect the benzoxazine reactivity as well, were studied.

Thermal properties of the resulting thermosets showed unexpected stabilities and high char yields, higher than 50%, for this class of materials. Both coumarin-containing thermosets showed T_g in the range between 160 and 190 °C, being these values higher than the respective T_g for the unsubstituted **PH-a**.

The coumarin-containing benzoxazine resins reported in this work have been demonstrated to be competitive starting materials comparable to other petroleum-based benzoxazine resins toward the generation of useful thermoset materials.

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