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Renewable Thermosetting Resins and Thermoplastics from Vanillin

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Abstract

Two cyanate ester resins and a polycarbonate thermoplastic have been synthesized from vanillin. The bisphenol precursors were prepared by both an electrochemical route as well as by a McMurry coupling reaction. 1,2-bis(4-cyanato-3-methoxyphenyl)ethene (**6**) had a high melting point of 237 °C and did not cure completely under a standard cure protocol. In contrast, the reduced version, 1,2-bis(4-cyanato-3-methoxyphenyl)ethane (**7**) melted at 190 °C and underwent complete cure to form a thermoset material with T_g = 202 °C. **7** showed thermal stability up to 335 °C and decomposed via formation of phenolics and isocyanic acid. A polycarbonate was then synthesized from the reduced bisphenol by a transesterification reaction with diphenylcarbonate. The polymer had M_n = 3588, M_w/M_n = 1.9, and a T_g of 86 °C. TGA/FTIR data suggested that the polycarbonate decomposed via formation of benzodioxolanes with concomitant elimination of methane. The results show that vanillin is a useful precursor to both thermosetting resins and thermoplastics without significant modification.

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Introduction

Oil is a remarkably versatile raw material for the production of fuels, polymers, and commodity chemicals. Unfortunately it is also a finite resource and understanding of this limitation has led to extensive research on sustainable feedstocks that can supplement and eventually replace petroleum.[1-9] The most important sustainable feedstock, due to its abundance, is lignocellulosic biomass which is composed primarily of the three biopolymers cellulose, hemicellulose, and lignin. In regard to high-performance polymers, lignin is the most compelling feedstock as it is essentially composed of "trapped" phenolic compounds. A variety of polymers have been prepared from lignin including phenol-formaldehyde resins, polyolefin/lignin blends, polyesters, polyurethanes, and bioplastics.[10] Lignin has also been examined as a feedstock to phenolic monomers that can be utilized in a similar manner to petroleum-derived phenols. However, lignin is a very complex biomolecule and differs significantly between plant species. For example, in coniferous trees guaiacyl units predominate, whereas in deciduous trees syringyl units are more common. The guaiacyl units can be readily oxidized to vanillin, while the syringyl units yield syringaldehyde[11] (Figure 1).

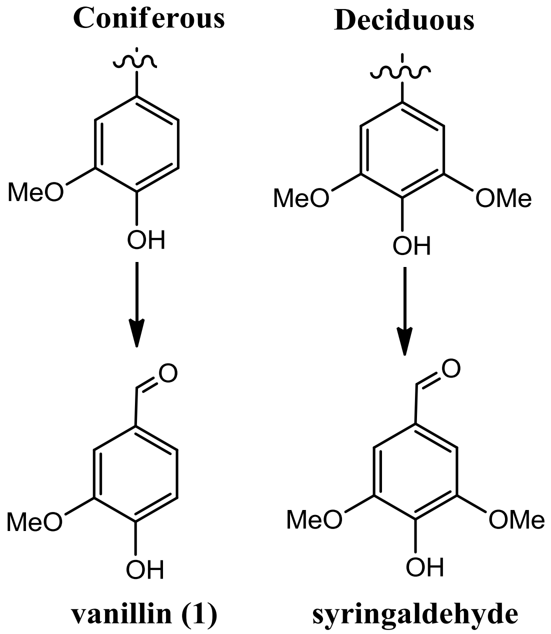

Figure 1. Conversion of guaiacyl and syringyl units to vanillin and syringaldehyde

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Perhaps the best known sustainable phenol is vanillin. Natural vanillin can be derived from the vanilla bean through hydrolysis of vanillin glucoside and is also present in trace amounts in a variety of plants including tobacco. In 1874 a process was developed for the conversion of eugenol (derived from clove oil) to vanillin.[11,12] The search for cheaper feedstocks led to the production of vanillin from waste sulfite liquor available as a byproduct of paper pulping. This process was practiced in Canada until 1987 and the United States until 1991. Borregaard Industries, a Norwegian company, still produces vanillin and ethyl-vanillin from wood. Despite the availability of vanillin from renewable sources, the bulk of synthetic vanillin is currently prepared from petroleum with guaiacol serving as an intermediate.[10]

The use of vanillin as a precursor to polymeric materials has recently been studied. For example, hydrogenation of vanillin to 2-methoxy-4-methylphenol followed by condensation with aldehydes has been shown to yield bisphenols that can be converted to cyanate ester resins with high glass transition temperatures and good thermal stability.[13] Other recent work has shown that bivanillin can be electrochemically polymerized to polyvanillin,[14] while a follow-on study examined Schiff-base vanillin polymers for metal chelation.[15] Thermosetting vinyl esters based on vanillin have been reported,[16] as well as vanillin-based PET mimics[17] and vanillin-fatty acid polymeric systems.[18]

To generate thermoplastics such as polycarbonates and thermosetting resins from vanillin, bisphenols are required. In a seminal 1952 paper, Pearl described the electrochemical reductive dimerization of vanillin to hydrovanilloin (**2**).[19] Although this is an important first step, the vicinal diols must be reductively eliminated to generate a useful monomer. Pearl accomplished this task by a multi-step process that involved $Cu(OH)_2$ oxidation of hydrovanilloin to vanillil, followed by zinc reduction to desoxyvanilloin and finally Raney nickel reduction to 4,4’-dihydroxy-3,3’-dimethoxystilbene (Compound **4**, Scheme 1).[20] This cumbersome method was not practical, especially for the large scale preparation of the bisphenol, and a subsequent patent reported the direct catalytic hydrogenation of hydrovanilloin to generate 4,4’-dihydroxy-3,3’-dimethoxy-diphenylethane (**5**). However, despite the promise of this approach, high catalyst loadings (6 g PtO_2/30 g hydrovanilloin), and/or harsh conditions (175 °C, 150-170 atm, copper chromite catalyst) limit the effectiveness of this more direct route.[21] Moreover, despite the availability of bisphenol **5** for more than 60 years, there have been no reports of thermoplastics or thermoset resins prepared from **5** with the exception of a patent describing the relevant epoxy resins.[22] Due to the attractiveness of vanillin as a fully renewable and sustainable feedstock, our group became interested in developing new synthetic methods for the preparation of **4**. In addition, it was of interest

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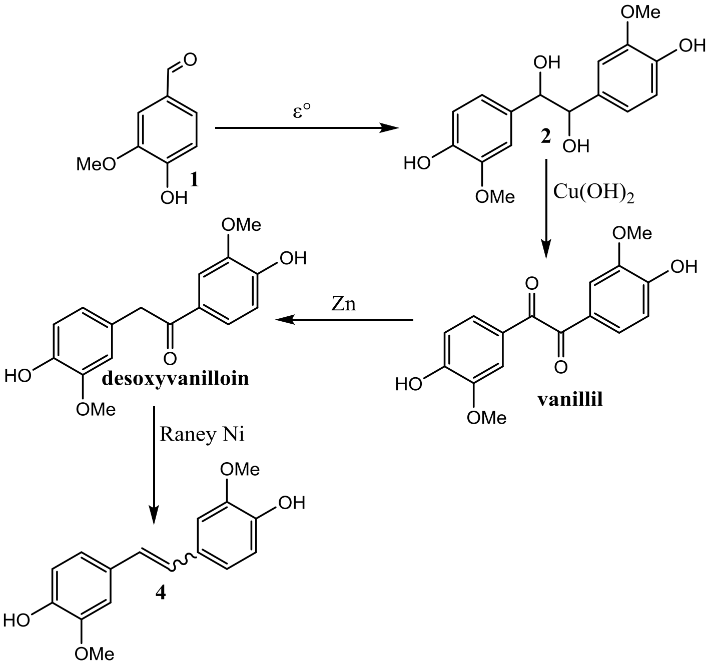

Scheme 1. Pearl's original synthesis of a bisphenol from vanillin

to synthesize thermoplastic and thermoset materials from **5**. This paper describes these efforts as well as the properties of the resulting renewable resins.

Experimental

General methods. McMurry reactions were carried out using standard Schlenk techniques. THF and triethylamine were both distilled from Na/benzophenone prior to use. Vanillin, platinum oxide (PtO_2), titanium tetrachloride, and cyanogen bromide were purchased from Aldrich and used as received. ^{1}H and ^{13}C NMR measurements were performed using a Bruker AC 300 or Bruker 400 MHz instrument. ^{1}H and ^{13}C NMR chemical shifts are reported versus the deuterated solvent peaks [$CDCl_3$: δ 7.27 ppm (^{1}H), 77.23 ppm (^{13}C). DMSO-d_6: δ 2.50 (^{1}H), 39.51 (^{13}C). DMF-d_7: 8.03 (^{1}H), 163.15 (^{13}C)]. Infrared analysis was performed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy with a single bounce diamond ATR crystal. The instrument used was a Nexus 870 FTIR spectrometer with a liquid N_2 cooled mercury cadmium telluride (MCTA) detector. Each spectrum is an average of 28 scans at 4 cm^{-1} resolution. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Hydrovanilloin (2): In a 1-liter beaker vanillin (**1**) (40.32 g, 0.26 mol) and sodium hydroxide (40.29 g, 1.0 mol) were dissolved in water (600 mL) with slight heating and stirring. Once the solids were completely dissolved, a working electrode made of lead and having approximate dimensions of 4”x4”x1/8” was

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inserted into the beaker. The auxillary electrode was a piece of lead measuring 4”x6”x1/8” that was rolled up and placed in a secondary coarse fritted flask. A potential of -2 Volts (vs. Ag/AgCl) was applied with a current of 1.5 amps. The reaction was allowed to proceed for 5 h, then the electrodes were removed and the solution was acidified using concentrated HCl. The product precipitated as a white solid, was isolated by filtration, and washed with copious amounts of water. Drying the solid overnight under reduced pressure yielded 27.56 g of product (90 mmol, 69%). ^{1}H NMR (d$_6$-DMSO) δ 8.67 (s, 2H), 6.72 (d, 2H, J=1.3 Hz), 6.61 (m, 4H), 4.923 (s, 2H), 4.42 (s, 2H), 3.62 (s, 6H). ^{13}C NMR (d$_6$-DMSO) δ 55.92, 77.39, 112.16, 114.76, 120.32, 134.62, 145.62, 147.03.

1,2-bis(4-acetoxy-3-methoxyphenyl)ethane-1,2-diyl diacetate (3): 2 (1.40 g, 5 mmol) was dissolved in 50 mL of acetic anhydride and 2 mL pyridine. The reaction was refluxed under nitrogen for 1 h. The solvent was then removed under reduced pressure to yield a tan solid. The solid was washed with water (3x5 mL) and ethyl acetate (2x5 mL) and then dried under reduced pressure. This procedure yielded 1.55 g of product (3 mmol, 72%). ^{1}H NMR (d$_6$-DMSO) δ 7.00 (d, 2H, J=6 Hz), 6.77 (m, 4H), 5.99 (s, 2H), 3.63 (s, 6H), 2.48 (t, 6H, J=1.8 Hz), 2.21 (s, 6H). ^{13}C NMR (d$_6$-DMSO) δ 20.36, 20.69, 55.67, 75.37, 111.82, 119.45, 122.39, 134.72, 139.09, 150.28, 168.46, 169.27. Anal. Calcd for $C_{24}H_{26}O_{10}$: C, 60.76; H, 5.52. Found: C, 61.01; H, 5.59.

(*E*)-4,4'-(ethene-1,2-diyl)bis(2-methoxyphenol) (4) (reduction of 3 with zinc): 3 (0.56 g, 1 mmol), Zn powder (2.14 g, 33 mmol), and NaOH (0.5 g, 12.5 mmol) were added to a flask. The mixture was slurried in 20 mL of a 50:50 solution of ethanol:water and then heated to reflux under nitrogen for 3.5 h. The solution was decanted leaving residual zinc powder in the flask and the remaining solution was acidified to pH 4 using 2M HCl. The resulting tan precipitate was filtered, washed several times with water, and dried under reduced pressure to yield 170 mg of product (0.6 mmol, 47%). The ^{1}H NMR spectrum was consistent with the literature[23] and with the product generated by other means (*vide infra)*.

(*E*)-4,4'-(ethene-1,2-diyl)bis(2-methoxyphenol) (4) (McMurry coupling). A flask was charged with Mg (2.35 g, 96.7 mmol) and anhydrous THF (100 mL). The mixture was chilled to -78 °C and then $TiCl_4$ (10.6 mL, 96.5 mmol) was added dropwise through an addition funnel. The flask was allowed to slowly warm up to room temperature and the mixture transitioned to a green slurry and finally a black solution. After stirring at room temperature for 30 min a THF (50 mL) solution of vanillin (7.01 g, 46.1 mmol) was added dropwise. The reaction was mildly exothermic and resulted in a dark brown mixture. The mixture was heated at reflux for 3 h and was then cooled to room temperature. The solvent was removed under reduced pressure and the residue treated with HCl (100 mL, 2 M) to yield a dark solution with pale brown suspended solid. The mixture was filtered on a medium frit and the isolated solid was washed with water (3 x 50 mL) and chilled ethanol (3 x 25 mL, 0 °C). The solid was dried in a vacuum oven (~10 Torr, 45 °C) overnight to yield 2.91 g of pale brown solid (46% yield). The purity of the crude product (>98%) was suitable for later synthetic procedures, but the material can be further purified by dissolution in THF followed by precipitation with hexane. X-ray quality crystals were grown by slow evaporation of a concentrated THF solution. ^{1}H NMR (DMSO-d_6): δ 9.07 (s, 2H, Ph-OH), 7.13 (d, 2H, *J* = 2 Hz), 6.94 (s, 2H), 6.93 (dd, 2H, *J* = 8, 2 Hz), 6.73 (d, 2H, *J* = 8 Hz), 3.81 (s, 6H, OMe); ^{13}C NMR (DMSO-d_6): δ 147.8, 146.2, 129.2, 125.8, 119.5, 115.6, 99.6, 55.6.

4,4'-(ethane-1,2-diyl)bis(2-methoxyphenol) (5). A Parr reaction vessel was charged with **4** (2.85 g, 10.5 mmol), THF (50 mL), PtO_2 (70 mg), and then placed under a hydrogen atmosphere (30 psig) and allowed to react at ambient temperature for 16 h with continuous agitation. The mixture was filtered through glass wool to remove platinum and the THF was removed under reduced pressure. The solid was washed with hexanes (2 x 30 mL) and dried under reduced pressure to afford 2.62 g of light brown solid (91% yield). ^{1}H NMR (DMSO-d_6) δ 8.66 (s, 2H, Ph-OH), 6.73 (s, 2H), 6.65-6.53 (m, 4H), 3.70 (s, 6H, OMe), 2.70 (s, 4H, CH_2); ^{13}C NMR (DMSO-d_6): δ 147.7, 144.9, 133.1, 120.9, 115.6, 113.1, 56.0 (OMe), 37.6 (CH_2).

(*E*)-1,2-bis(4-cyanato-3-methoxyphenyl)ethene (6). A flask was charged with **4** (0.70 g, 2.6 mmol), THF (30 mL), and CNBr (0.69 g, 6.5 mmol). The solution was chilled to -78 °C and triethylamine (0.75 mL, 5.5 mmol) was then added dropwise by syringe. The pale brown solution was allowed to warm to room temperature and a tan solid precipitated. After stirring at ambient temperature for 20 min, the slurry was filtered and the solid was collected on a medium glass-frit. The solid was washed with water (3 x 20 mL) and air dried to yield 640 mg (77%) of the crude product. Recrystallization from hot THF yielded 530 mg of off-white needles. Crystals suitable for an X-ray diffraction study were grown by slowly cooling a concentrated acetonitrile solution. ^{1}H NMR (DMF-d_7) δ 7.66 (d, 2H, *J* = 2 Hz), 7.60 (d, 2H, *J* = 9 Hz), 7.50 (s, 2H, -CH=CH-), 7.35 (dd, 2H, *J* = 9, 2 Hz), 4.07 (s, 6H, OMe)

1,2-bis(4-cyanato-3-methoxyphenyl)ethane (7). A flask was charged with **5** (1.05 g, 3.8 mmol), THF (40 mL), and CNBr (1.06 g, 10 mmol). The flask was cooled to -20 °C and triethylamine (1.16 mL, 8.4 mmol) was added dropwise. A tan solid immediately precipitated from solution. The mixture was stirred at -20 °C for 10 min and was then removed from the cold bath and allowed to spontaneously warm. After stirring for an additional 30 min, the mixture was filtered on a medium glass-frit and the solid washed with water (3 x 20 mL) and then air dried to yield 0.71 g of crude product. Evaporation of the filtrate followed by water and ether washes yielded an additional 0.22 g of product for a total of 0.93 g (76%).

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Recrystallization from hot THF yielded 625 mg of tan needles. ^{1}H NMR (DMSO-d_6) δ 7.42 (d, 2H, J = 8 Hz), 7.18 (s, 2H), 6.91 (d, 2H, J = 8 Hz), 3.88 (s, 6H, OMe), 2.91 (s, 4H, CH_2). Anal. Calcd for $C_{18}H_{16}O_4N_2$: C, 66.86; H, 4.97. Found: C, 66.67; H 4.96.

Polycarbonate Synthesis. **5** (0.4 g, 1.46 mmol), diphenyl carbonate (0.34 g, 1.59 mmol) and $Zn(Ac)_2\cdot 2H_2O$ (8.5 mg, 2.5 mol%) were combined in a flask. The flask was heated to 190 °C under N_2 for 4 hours. While maintaining this temperature, the flask was then placed under reduced pressure (~30 torr) for 2 h. The pressure was then further reduced to ~1 torr and the mixture left to react at 190 °C overnight. The resulting resinous solid was allowed to cool to room temperature, and was then dissolved in CH_2Cl_2, filtered, and precipitated in methanol. This process was repeated and the resulting pale yellow solid was then dried under reduced pressure (Yield: 0.30 g, 69%). ^{1}H NMR[24] ($CDCl_3$) δ 7.14 (d, 2H, J = 8 Hz, Ph), 6.77(d, 2H, J = 8 Hz, Ph), 6.69 (s, 2H, Ph), 5.49 (bs, residual –OH, endcap), 3.82 (s, 6H, OMe), 2.91 (bs, 4H, -CH_2)

Cyanate Ester Test Sample Preparation. Silicone molds were degassed at 95 °C and 30 torr prior to use. Sample discs measuring 12 mm in diameter x 1-3 mm thick were fabricated by melting the uncatalyzed monomer in the mold and curing under flowing nitrogen for 1 h at 150 °C followed by 24 h at 210 °C. The temperature ramp rate during cure was 5 °C / min. The resultant discs weighed 0.2-0.4 g.

Physical Analysis. Differential scanning calorimetry was performed on ~10 mg samples of monomer using a TA Instruments Q200 calorimeter under 50 mL / min. of flowing nitrogen. Samples were heated to 350 °C, cooled to 100 °C and re-heated to 350 °C, all at 10 °C / min. Cured discs were tested via dynamic thermomechanical analysis (dynamic TMA) with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were held in place via a 0.2 N mean compressive force with the standard ~5 mm diameter flat cylindrical probe while the probe force was modulated at 0.05 Hz over an amplitude of 0.1 N and the temperature was ramped to 350 °C at 10 °C / min. These rapid heating rates were needed to minimize post-cure of the samples during testing. The thermal lag for each sample was determined (using temperature limits of 100 °C and 200 °C) and used to correct the TMA thermocouple readings (typically by about 5 °C) via a temperature cycling procedure described in detail elsewhere.[25]

Analysis by TGA-FTIR. Thermal gravimetric analysis (TGA) - Fourier Transform Infrared (FTIR) analyses were performed using a Nicolet Nexus 870 FTIR spectrometer interfaced by a heated gas cell and transfer line (held at 150 °C) to a TA instruments Q50 TGA. The FTIR was programmed to acquire a

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spectrum every 10 seconds, integrating 8 scans per spectrum and 256 scans for the background. The TGA was ramped at 10° C/min to 200°C then 2 °C/min to 400 °C.

Results and Discussion

As a first step to explore the utility of vanillin-derived bisphenols, the electrochemical reductive coupling of vanillin was attempted using Pearl's method. This quick and relatively efficient method was capable of producing preparative scale quantities (~30 g) of the diol within several hours. However, despite claims in the patent literature to the contrary, we found the diol recalcitrant to reduction with moderate amounts of PtO_2 under 50 psi H_2 in acetic acid.[26] In part this lack of reactivity may be due to the low solubility of the diol in acetic acid. To improve the solubility and lower the reduction potential of the vicinal alcohols,[27,28] we synthesized the tetracetate from the diol. Attempts to reduce this compound were also unsuccessful under moderate conditions, both with PtO_2 under a H_2 atmosphere and with Pd/C and ammonium formate in refluxing acetic acid. On one occasion after unsuccessfully reducing the tetra-acetate, an attempt was made to recover the diol from the reaction mixture by a base workup. Surprisingly, instead of recovering the diol, **4** was isolated in 34% yield by the elimination of the acetates. This result was unexpected given the basic conditions, but is analogous to the formation of **4** from 1,2-bis(4-hydroxy-3-methoxypheyl)-1,3-propanediol under both alkaline[29-32] and acidic[33] conditions. To improve the yield of the reduction, the use of zinc was considered. Metallic zinc has been shown to facilitate the pinacol elimination of water from vicinal diols followed by subsequent reduction to conjugated systems.[34] Zinc has also been shown to reduce stilbene epoxides to alkenes.[35] Under the same basic deprotection conditions, use of excess zinc increased the yield of the trans-stilbene to nearly 50%. A plausible mechanism involves attack by hydroxide to yield an intermediate epoxide that is then reduced to the alkene (Scheme 2). Thus, instead of the 4-step process for conversion of vanillin to the stilbene developed by Pearl, a new 3-step method has been discovered.

Although the electrochemical method was promising, a more direct route was of interest and the stilbene was synthesized via a McMurry coupling by reaction of vanillin with $TiCl_4$/Mg in THF (Scheme 3). A 2004 study showed that reaction of vanillin with a McMurry reagent generated from $TiCl_3$/Zn, gave a 40% yield of **5** and a 36% yield of a 60:40 Z/E mixture of the stilbene.[36] The direct conversion of hindered ketones to reduced stilbenes has also been observed with the $TiCl_3/LiAlH_4$ reagent[37] and organometallic [Ti]/$LiAlH_4$ catalysts have been shown to be active for the hydrogenation of alkenes.[38,39] In contrast, the use of magnesium as the reducing agent did not promote hydrogenation of the alkene

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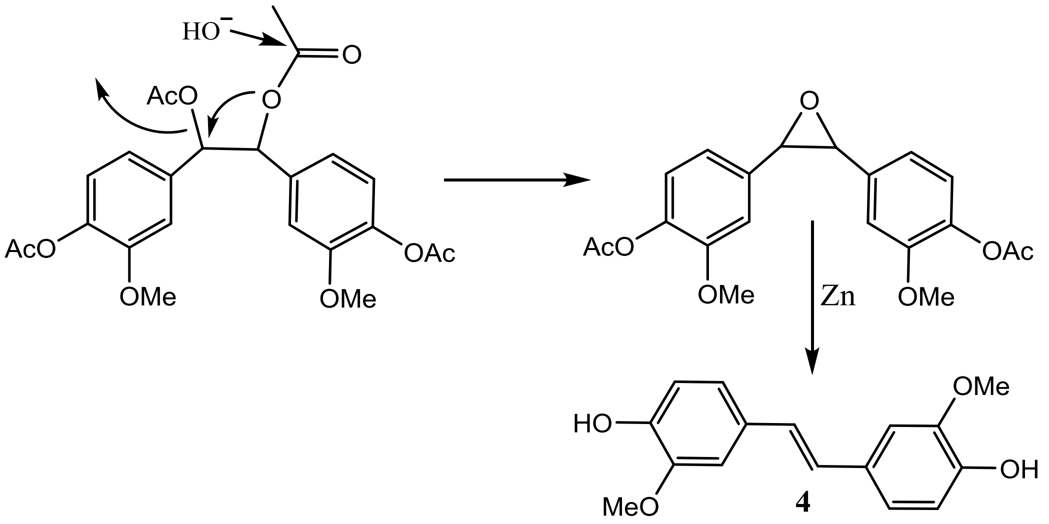
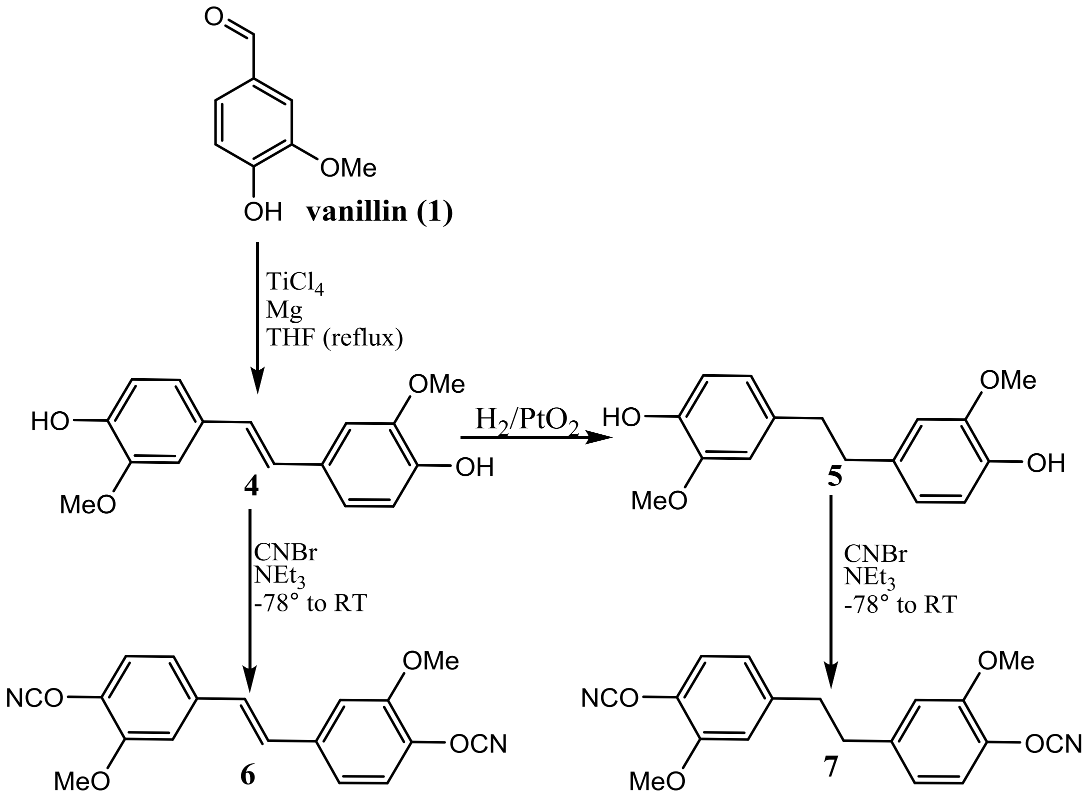


Scheme 2. Proposed mechanism for the base catalyzed elimination of vicinal diacetates followed by reaction with zinc to yield the stilbene **4**



Scheme 3. Synthesis of bisphenols and cyanate esters from vanillin

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and allowed the isolation of the pure trans-olefin in 46% yield without chromatography or recrystallization. The saturated bisphenol was then readily prepared by catalytic hydrogenation with PtO_2 under modest conditions (30 psig H_2, ambient temperature).

With **4** and **5** in hand, cyanate esters were synthesized from both compounds (Scheme 3). The cyanate esters exhibited low solubility in THF and other common organic solvents which allowed for their isolation in good yield by a simple filtration and water wash. High quality crystals of both **6** and **7** were obtained and this allowed an examination of their structures by single crystal X-ray diffraction (Figure 2). The bond lengths and angles of **6** and **7** are quite typical of cyanate esters, but intermolecular

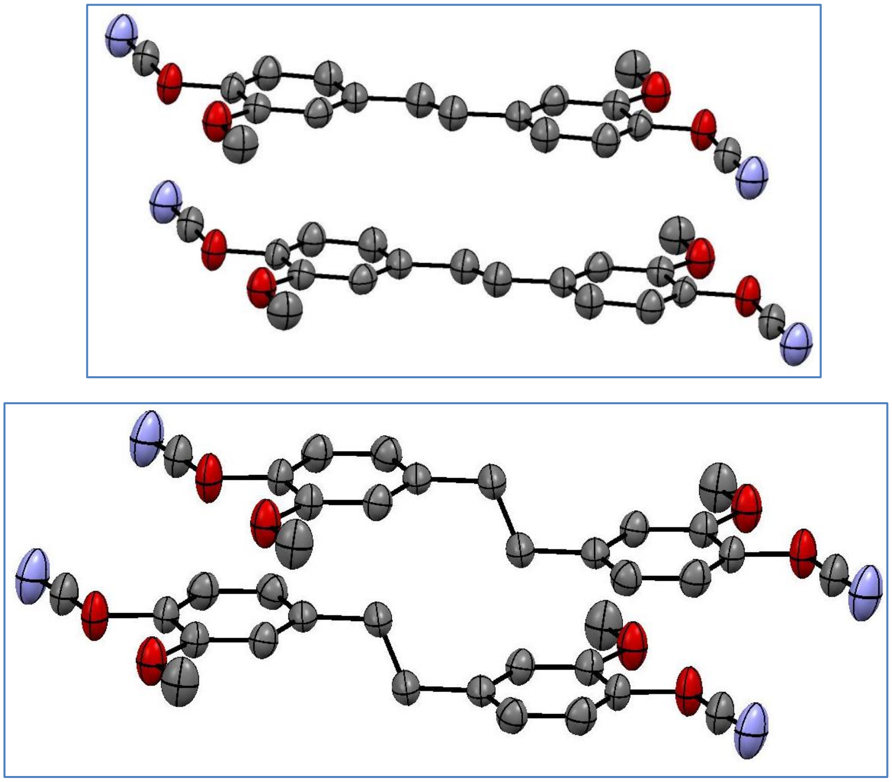

Figure 2. X-ray crystal structures showing the pi-stacking of compound **6** (top) and **7** (bottom). Partial molecules in the unit cell and hydrogen atoms have been omitted for clarity

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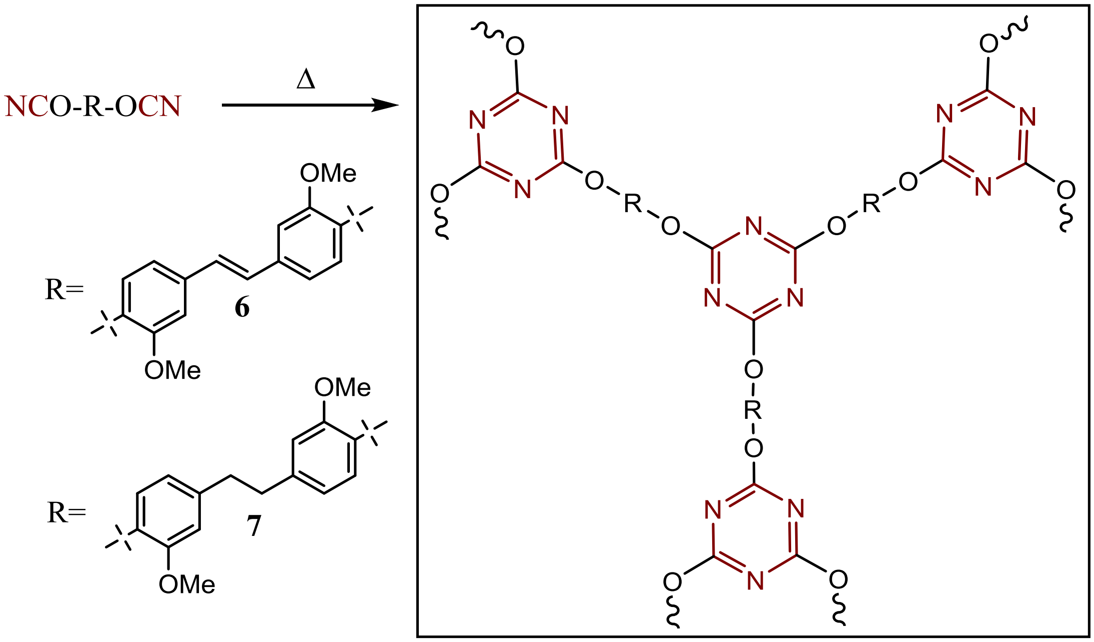
forces in the solid state have an impact on the melting points and ultimately the cure chemistry of these resins. Given that efficient curing can only occur in the liquid phase, a lower melting point is beneficial as it translates into a larger processing window for the material. Although **6** and **7** both crystallize in the P 1 21/c 1 space group and have similar molecular weights, their melting points of 237 and 190 °C, respectively, are quite disparate. Starting first with **6**, a planar molecule, one can observe from the X-ray data (Figure 2 and ESI)[40] that the aromatic rings stack in a parallel-displaced conformation with a centroid-to-centroid distance of 3.877(3) Å and an interplanar distance of 3.551(3) Å. The aromatic rings in **7** stack in a similar conformation, but the sp^3 hybridization of the bridging carbons and anti-configuration of the attached hydrogens results in a much longer centroid-to-centroid distance of 4.401(2) Å and a shorter interplanar distance (aromatic rings) of 3.520(2) Å. Based on the structural data, it seems likely that the conjugated pi-stacking in **6** is a significant contributor to the increased melting point of the solid.

After fully characterizing **6** and **7**, the thermal conversion of the monomers to polycyanurates (Scheme 4) was investigated by DSC. The thermal curing of **6** proved challenging due largely to its high melting point. DSC analysis of the monomer showed a sharp melting transition at 237 °C and a large enthalpy of melting of 230 J/g along with a melt-triggered exotherm of 160 kJ/mol-equiv cyanate ester (Figure 3).



Scheme 4. Thermal cyclotrimerization of bis(cyanate) esters to form polycyanurates

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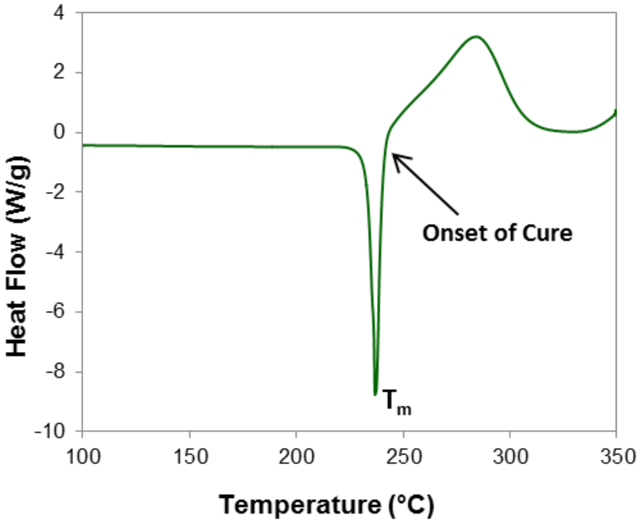

Figure 3. DSC data for compound **6**

Since this value is considerably larger than typically seen for curing of cyanate ester groups (~100 kJ/mol-equiv),[41] it is likely that additional chemical reactions take place concomitant with cyclotrimerization. After heating the sample and allowing the cure/reaction chemistry to finish, no glass transition was observed in the DSC curve. As expected, when a sample of **6** was loaded in to a silicone mold large enough to accommodate compaction and was then heated to 150 °C at 300 torr under a nitrogen purge, no consolidation of the sample was observed. Further heating of the sample to 210 °C under 15 psi of nitrogen also resulted in no visible consolidation of the sample. After 24 h at 210 °C, the partly consolidated sample was removed from the mold and analyzed by FT-IR spectroscopy. The FT-IR data indicated a conversion of 50-70% based on the disappearance of the cyanate ester monomer band; however, the cyanurate peaks in the spectrum were somewhat smaller than expected. Although the cure chemistry of **6** renders it unsuitable as a standalone resin, blending it with a liquid cyanate ester resin or other comonomer to depress its melting point and allow for a low temperature cure protocol may offer a method for direct utilization of **6** in composite materials.

In contrast to the results obtained for **6**, samples of monomer **7** were found to consolidate and cure in a much more favorable manner. The DSC of **7** (Figure 4) was more typical of easily processed cyanate esters, although the observed melting point near 190 °C is higher than normal and results in a smaller, though still ample process window, with a cure exotherm commencing shortly after the sample appears fully melted. The DSC measured cure exotherm of 92 kJ/mol-equiv cyanate ester is close to the

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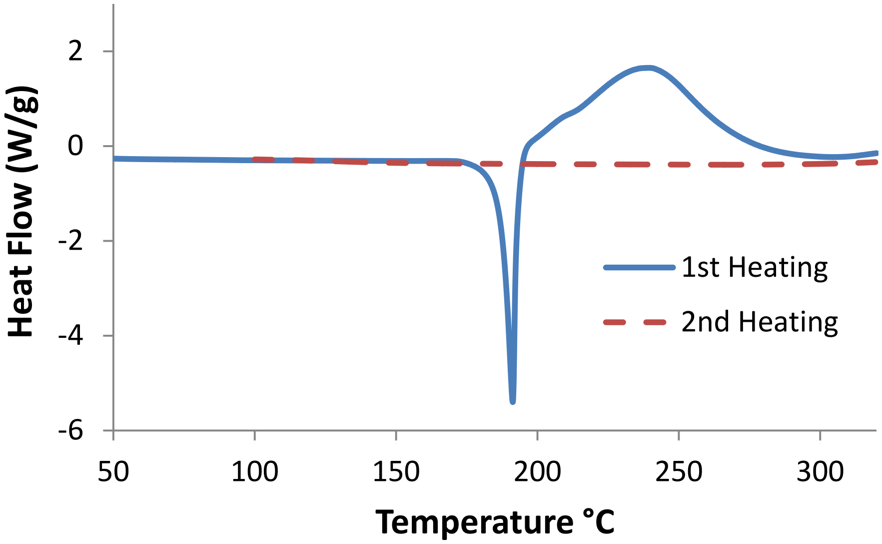

Figure 4. DSC data for compound **7**

expected 100 kJ/mol-equiv cyanate ester and suggests that the cure reaction proceeds to completion. When the powder was placed in a silicone mold and heated to 210 °C for 24 h, the sample was able to melt and compact over a period of a few minutes, well before the onset of significant cyclotrimerization, resulting in the formation of a void-free sample as cure proceeded. A DSC analysis of the as-molded

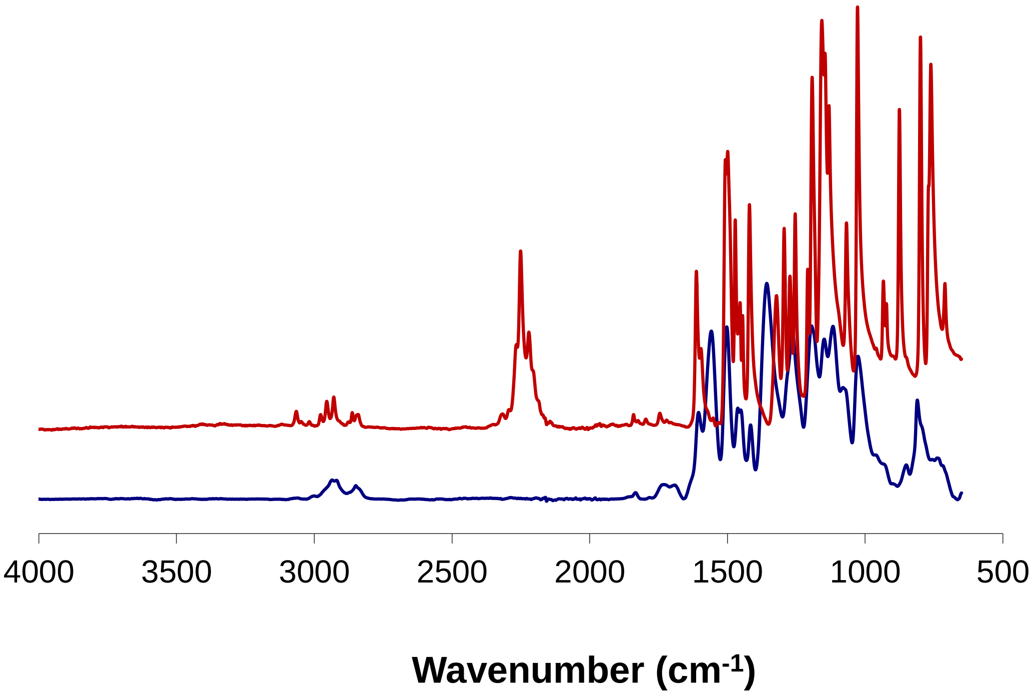

Figure 5. FTIR data for compound **7** (red) and the cured resin (blue)

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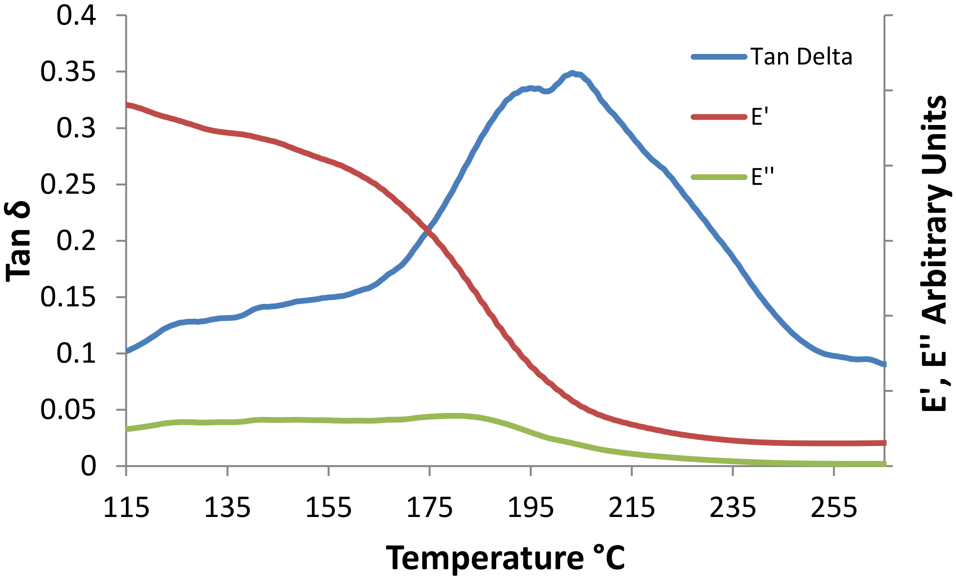

Figure 6. TMA data for compound **7**. E' and E" are the apparent loss and storage moduli, respectively.

sample revealed no detectable residual cure. Moreover, FT-IR analysis indicated an extent of cure of approximately 98% (Figure 5). The high quality of the sample allowed for a more in-depth analysis of the thermomechanical properties of cured **7** via TMA (Figure 6). The sample shows a peak in the loss modulus at 180 °C with a corresponding peak in tan-δ of 202 °C. This value is relatively low compared to the cyanate ester derived from bisphenol A (as-cured Tg of 275 °C[42]) due to the 2-carbon bridge between aromatic rings. However the T_g is comparable to high performing epoxy resins and is intermediate between the T_g of a recently described renewable cyanate ester with a 4-carbon bridge between aromatic rings (186 °C)[43] and bis(cyanate) esters derived from creosol with single carbon linkages between rings (230-250 °C).[13]

The thermal stability and cure chemistry of both cyanate esters was further explored using an inline FTIR spectrometer coupled to a TGA instrument. **6** began to liberate THF at around 160 °C with 10% weight loss obtained by 205 °C. THF is also observed in the NMR spectrum of the molecule suggesting that significant amounts of the solvent are trapped during crystal formation. The weight of the sample was relatively stable between 205 and 270 °C with an additional weight loss of only 3%, but the weight loss then began to rapidly accelerate with a total weight loss of 27% at 350 °C (Figure 7). The gas phase FTIR spectrum at 390 °C showed primarily formation of isocyanic acid (Figure 8). In light of the DSC and FTIR

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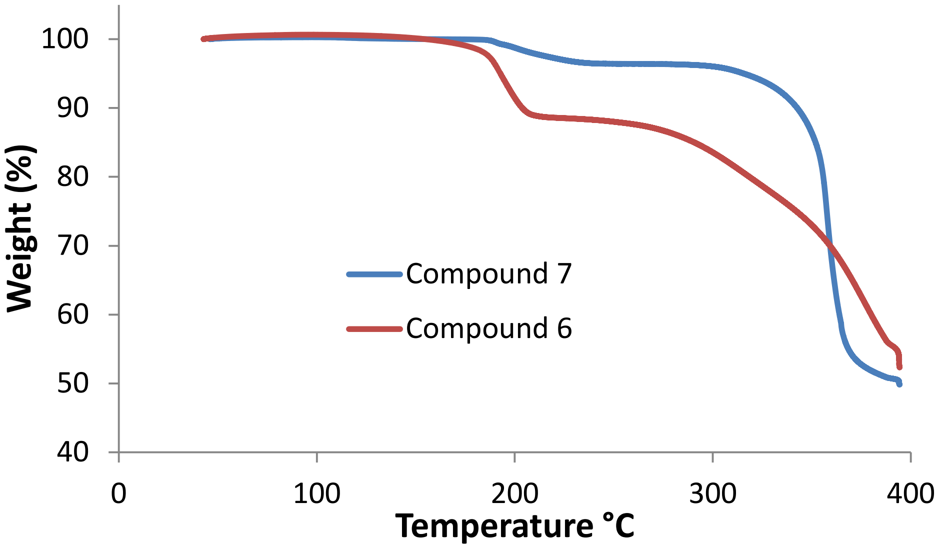

Figure 7. TGA data for compounds **6** and **7**

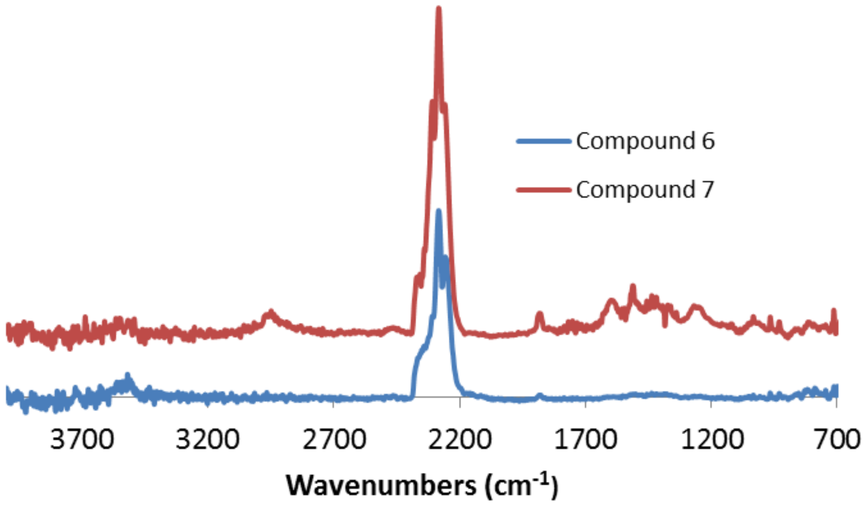

Figure 8. Gas phase IR spectra of the thermal decomposition products of **6** and **7** at 390 °C.

data discussed above, it seems clear that cyclotrimerization is in competition with decomposition of the parent molecule. This effect is driven by the high melting point of **6** which doesn't allow for significant cyclotrimerization below 237 °C. In contrast, **7** exhibited only a 3% weight loss starting at about 190 °C, the melting point of the crystalline material. Similar to **6**, FTIR analysis shows that this initial weight loss was due to evolution of trapped THF. The weight of the sample was then stable up to well above 300 °C,

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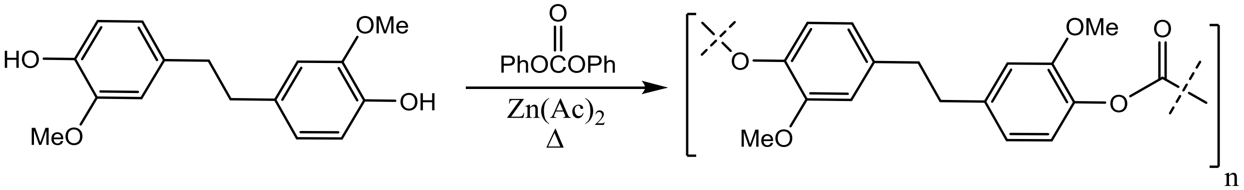
exhibiting 5% weight loss at 335 °C and 10% weight loss at 350 °C. The gas phase FTIR spectrum (Figure 8) showed evolution of primarily isocyanic acid along with some traces of phenolic fragments generated by cleavage of the aliphatic bridging group between aromatic rings. Although the thermal stability of **7** is not comparable to conventional cyanate esters, the decomposition occurs at significantly higher temperatures than the T_g and should not affect the use temperature of the resin.

To expand the chemistry of **5** to include a thermoplastic material, a polycarbonate was synthesized from the reduced bisphenol by transesterification with diphenyl carbonate (Scheme 5). This synthetic route gave a resin with $M_n = 3588$ as determined by GPC, and a polydispersity of 1.9. ^{1}H NMR analysis (Figure S3-ESI) showed that the resin was end-capped by hydroxyl groups (peak at 5.5 ppm) and comparison of the methoxy and hydroxy integrals gave a molecular weight of ~4035 or roughly 13 repeat units. The T_g of the resin was 86 °C which reflects the relatively low molecular weight of the resin and the greater flexibility of the monomers compared to methylene or isopropylidene bridged monomers. As a comparison, a bisphenol A polycarbonate with a MW of ~3500 would be expected to have a T_g of ca. 120 °C.[44,45] The T_g of the vanillin-derived polycarbonate can also be compared to a recently described polycarbonate derived from eugenol with a 4-carbon bridge between aromatic rings and a T_g of 52 °C for a polymer of similar molecular weight.[46] No attempt was made to synthesize a higher molecular weight polycarbonate from **5**, but it is expected that conducting the transesterification reaction at a higher temperature or utilizing phosgene as the carbonate source would dramatically improve the degree of polymerization.

The thermal stability of the polycarbonate was evaluated by TGA (Figure 9). The polymer lost 5% of its mass by 290 °C and 10% of its mass by 318 °C. FTIR analysis of the volatile products generated from the TGA experiment showed evolution of methane and a product with an intense absorption at 1836 cm^{-1} (Figure S4-ESI). This intense peak likely results from benzodioxolanes that are formed as a result of the methoxy group *ortho* to the carbonate. A similar result was observed for eugenol-based polycarbonates.[43]



Scheme 5. Synthesis of a polycarbonate from **5**

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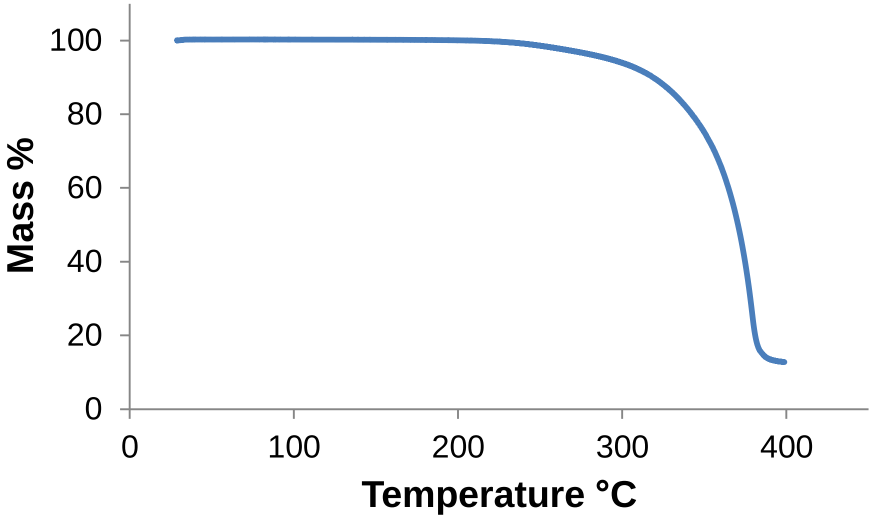

Figure 9. TGA data for the polycarbonate derived from **5**

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Conclusions

New polymers have been synthesized from the renewable phenol vanillin. Given the massive volume of lignin produced worldwide and the potential to generate vanillin from these sources in a sustainable fashion, the materials described in this work are potential green replacements for similar resins based on the ubiquitous bisphenol A. The functionality of vanillin, namely the presence of an aldehyde group, allows for the efficient synthesis of bisphenols and provides an example of how the diversity of biomass-derived phenols can actually improve their suitability as synthetic precursors. The (bis)cyanate ester (compound **7**) prepared from the reduced bisphenol **5** was amenable to thermal cure under modest conditions to yield a thermoset material with a T_g (202 °C) comparable to some of the highest-performing petroleum-derived epoxy resins. **5** was also readily converted to a polycarbonate with an acceptable T_g of 86 °C. Both the cyanate ester and polycarbonate resins showed similar decomposition behavior compared to other recently studied polymers with methoxy groups in the positions *ortho* to the original hydroxyl groups. This provides further evidence that these methoxy groups decrease the thermal stability of renewable resins by introducing lower temperature decomposition routes. Despite this behavior, these decomposition reactions occur at temperatures well beyond the T_gs and maximum use temperatures of the materials. Therefore, they are likely inconsequential for utilization of these resins under normal operating conditions.

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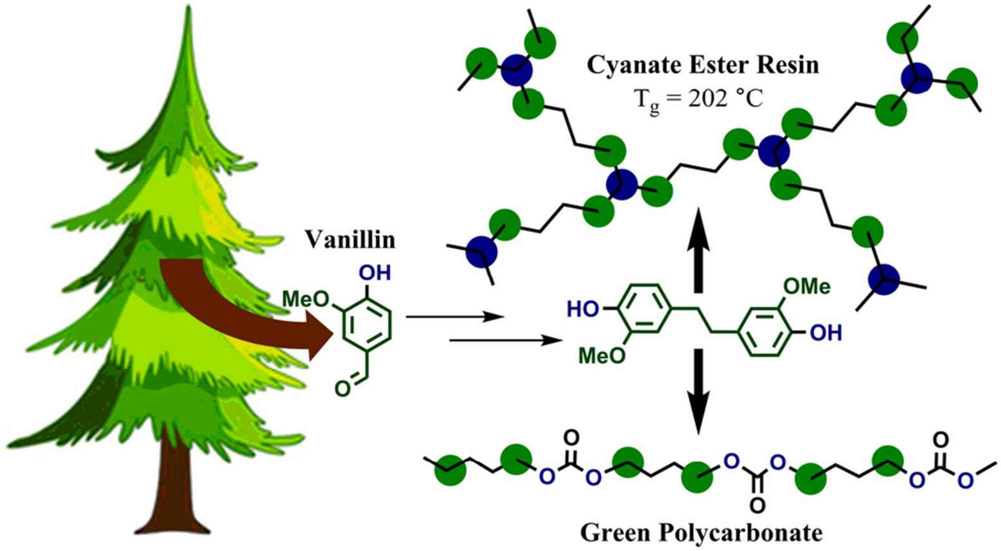

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