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## Sustainable Hydrophobic Thermosetting Resins and Polycarbonates from Turpentine

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### Abstract

Carvacrol is a renewable phenol that can be derived from abundant components of pine resin. To demonstrate the utility of carvacrol for polymer applications, a bisphenol was synthesized from carvacrol and converted to both a cyanate ester resin (**CarvCy**) and polycarbonate. A cured resin disk prepared from **CarvCy** exhibited a  $T_g$  of 224 °C and a water uptake of only 0.7% after being immersed in 85 °C water for four days. The wet  $T_g$  of the material was only 3 °C lower than the dry  $T_g$  showing that the cured resin was virtually unaffected by exposure to hot water. Despite the presence of aliphatic groups on the aromatic rings, the cured resin exhibited good thermal stability with only 5% weight loss at 390 °C. The polycarbonate prepared from carvacrol had  $M_n = 10,200$ ,  $M_w/M_n = 1.60$ ,  $T_g = 119$  °C, and even better thermal stability than the cyanate ester with 5% weight loss observed at 421 °C. The results provide compelling evidence that the sustainable phenol carvacrol can be used as a platform molecule for the generation of high performance polymers with exceptional properties.

## Introduction

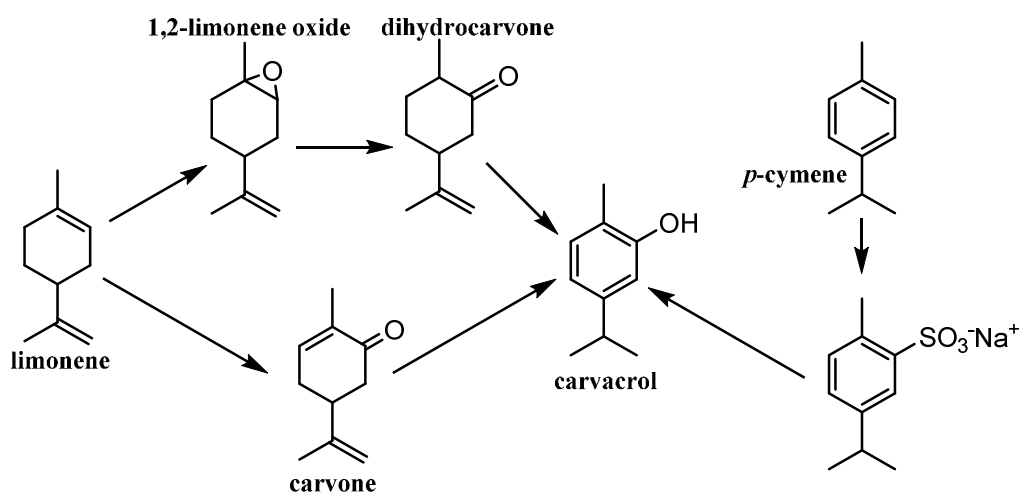
As the world population continues to increase and more pressure is exerted on the availability of natural resources including petroleum, the role of chemists is evolving. Sustainable feedstocks are becoming more important and the functionality of these feedstocks provides both challenges and opportunities to researchers. Polymers account for approximately 7% of total petroleum use and thus represent important targets for sustainable chemistry.<sup>1,2</sup> Over the last several years a number of researchers have investigated the conversion of renewable phenols from lignin and other biomass sources to bisphenols and derivative polymers.<sup>3-16</sup> These renewable bisphenols can be converted to a wide variety of resins including polycarbonates, epoxy resins, and cyanate ester resins.

Cyclic terpenes are another important source of renewable phenols. Although not as abundant as lignin, naturally occurring terpenoids, including *p*-cymene,  $\alpha$ - and  $\beta$ -pinene, are readily available in the form of turpentine.<sup>17</sup> Approximately 350,000 tons of turpentine are produced annually<sup>2</sup> with most of it generated as a byproduct of paper production. Limonene is another important terpene which is found in the skins of citrus fruit. Approximately 77 million kg of limonene are generated annually,<sup>18</sup> primarily as a byproduct of orange juice production. In addition to isolation from trees and other sustainable sources, terpenoids are readily accessible via biosynthetic routes in which metabolically engineered organisms produce the molecules from sugar substrates.<sup>19,20</sup> Utilization of lignocellulosic sugars and implementation of this approach on an industrial scale could legitimately allow for terpenoids to supplant various petroleum-based polymer feedstocks.

Terpenes are incredibly versatile molecules for the generation of polymers.<sup>1,2</sup> The reactive double bonds of terpenes such as  $\beta$ -pinene allow for direct polymerization,<sup>21,22</sup> while aromatic molecules such as *p*-cymene can be accessed via dehydrogenation.<sup>23-25</sup> Similarly, phenolic terpenoids such as carvacrol and thymol can be readily generated from terpenes by selective oxidation and isomerization reactions.

Carvacrol is a component of the essential oils of thyme<sup>26</sup> and oregano<sup>27,28</sup> and has previously been synthesized by a number of routes starting from various terpenoids (Scheme 1). One of the early routes involved reaction of *p*-cymene with concentrated sulfuric acid to generate the sulfonic acid salt. This salt was then fused with sodium hydroxide to generate carvacrol.<sup>29</sup> Another route could start by oxidation of limonene to carvone followed by isomerization to carvacrol with sulfated zirconia.<sup>30</sup> The classic route to carvone uses NOCl as the oxidizing agent,<sup>31</sup> but more recently, highly selective oxidation of limonene to carvone has been accomplished using a Cr-based MOF catalyst and *tert*-butyl hydrogen peroxide as the oxidant.<sup>32</sup> Limonene can also be selectively oxidized to 1,2-limonene oxide which is readily isomerized to dihydrocarvone.<sup>33</sup> Dihydrocarvone can then be oxidized to carvacrol with reagents including ferric chloride.<sup>34</sup>

To explore the use of carvacrol as a sustainable alternative to phenol, this paper describes the facile synthesis of a bisphenol by acid catalyzed coupling of carvacrol with 1,3,5-trioxane. The synthesis and characterization of both a thermosetting cyanate ester resin and thermoplastic polycarbonate derived from the bisphenol are then discussed and the properties of both polymers are compared to those of conventional resins.



Scheme 1. Routes to carvacrol from limonene and *p*-cymene

## Experimental

**General.** All reagents were purchased from Aldrich and used as received except for triethylamine which was distilled from sodium benzophenone under nitrogen. NMR spectra were collected with a Bruker Avance II 300 MHz NMR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported versus the deuterated solvent peak [ $\text{CDCl}_3$ :  $\delta$  7.27 ppm ( $^1\text{H}$ ), 77.23 ppm ( $^{13}\text{C}$ )]. FTIR spectra were collected on a Thermo Nicolet Nexus 870 FTIR. The FTIR spectra are an average of 32 scans at  $4\text{ cm}^{-1}$  resolution. Elemental analysis was performed by Atlantic Microlabs Inc. Norcross, GA.

**Synthesis of 4,4'-methylenebis(5-isopropyl-2-methylphenol) (1).** Carvacrol (10.00 g, 66.6 mmol) was combined with 1,3,5-trioxane (1.96 g, 21.8 mmol) and dispersed in water (60 mL). Concentrated HCl (15 mL) was added and the mixture was heated in an  $80\text{ }^\circ\text{C}$  oil bath for six h. The product of the reaction consolidated into a solid off-white mass. The mixture was cooled to room temperature and the supernatant decanted. The solid product was dissolved in  $\text{CH}_2\text{Cl}_2$  with mild heating and washed with water. The organic layer was dried over  $\text{MgSO}_4$ , concentrated under reduced pressure with mild heating, and placed in a  $-20\text{ }^\circ\text{C}$  freezer overnight. The product crystallized as fine white needles which were collected by filtration, washed with cold hexanes, and dried under reduced pressure to yield 5.71 g (55%) of product.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 6.75 (s, 2H, Ph), 6.62 (s, 2H, Ph), 4.51 (bs, 2H, -OH), 3.86 (s, 2H,  $\text{CH}_2$ ), 3.05 (sept,  $J = 6.8\text{ Hz}$ , 2H, CH), 2.14 (s, 6H, Me), 1.18 (d,  $J = 6.8\text{ Hz}$ , 12H, Me). Anal. Calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_2$ : C, 80.73; H, 9.03. Found: C, 80.49; H, 9.02.

**Synthesis of bis(4-cyanato-2-isopropyl-5-methylphenyl)methane (CarvCy).** A round-bottomed flask equipped with a magnetic stirbar was charged with **1** (650 mg, 2.0 mmol) and acetone (20 mL). The mixture was stirred until the solids dissolved. The flask was then cooled in a dry ice/acetone bath and CNBr (657 mg, 6.2 mmol) was added. Triethylamine (440 mg, 4.4 mmol, 2.2 equiv) was then added dropwise over 3 min. White solids precipitated after the addition. The cooling bath was removed and

the mixture was stirred at ambient temperature for 1.5 h. The mixture was partitioned between Et<sub>2</sub>O (50 mL) and H<sub>2</sub>O (50 mL). The organic phase was further washed with H<sub>2</sub>O (50 mL) followed by brine (50 mL). Next, the organic phase was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure leaving the product as a white crystalline solid (690 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.35 (s, 2H, Ph), 6.69 (s, 2H, Ph), 3.97 (s, 2H, CH<sub>2</sub>), 3.06 (sept, *J* = 6.8 Hz, 2H, CH), 2.20 (s, 6H, CH<sub>3</sub>), 1.22 (d, *J* = 6.8 Hz, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 150.8, 147.4, 135.5, 133.2, 123.5, 111.8, 109.5, 33.9, 29.3, 23.5, 15.0. Anal. Calcd for C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.21; H, 7.23; N, 7.73. Found: C, 76.05; H, 7.25; N, 7.75.

**X-ray Diffraction.** A specimen of **CarvCy**, approximate dimensions 0.177 mm x 0.225 mm x 0.334 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1464 frames were collected. The total exposure time was 4.07 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 35839 reflections to a maximum  $\theta$  angle of 32.67° (0.66 Å resolution), of which 7077 were independent (average redundancy 5.064, completeness = 99.4%,  $R_{\text{int}}$  = 3.58%) and 5584 (78.90%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 9.0471(6)$  Å,  $b = 17.5709(11)$  Å,  $c = 12.9430(8)$  Å,  $\beta = 109.2500(10)^\circ$ , volume = 1942.5(2) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 1461 reflections above  $20 \sigma(I)$  with  $4.674^\circ < 2\theta < 64.93^\circ$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.956.

The final anisotropic full-matrix least-squares refinement on  $F^2$  with 250 variables converged at  $R1 = 4.95\%$ , for the observed data and  $wR2 = 13.67\%$  for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was  $0.527 \text{ e}^-/\text{\AA}^3$  and the largest hole was  $-0.280 \text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.061 \text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was

1.239 g/cm<sup>3</sup> and F(000), 776 e<sup>-</sup>. A cif file for **CarvCy** has been deposited with the Cambridge Structural Database (deposition number CCDC 1424051).

**Polycarbonate synthesis (CPC1).** **1** (0.50 g, 1.6 mmol), diphenyl carbonate (0.36 g, 1.7 mmol) and Zn(Ac)<sub>2</sub>•2H<sub>2</sub>O (9.7 mg, .0442 mmol) were combined in a flask. The mixture was heated to 190 °C under N<sub>2</sub> and held at that temperature for 4 h. The pressure in the flask was then reduced to approximately 10 torr and the temperature was maintained for an additional 2 h. The pressure was then reduced to 1 Torr for 16 h. The flask was cooled to room temperature and the resulting yellow, resinous solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a 0.2 μm syringe filter, and concentrated to approximately 5 mL. The product was then precipitated in methanol, collected on a glass frit, and dried in a vacuum oven overnight. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.15 (s, 2H, Ph), 6.75 (s, 2H, Ph), 3.98 (bs, 2H, CH<sub>2</sub>), 3.07 (sept, *J* = 6.8 Hz, 2H, CH), 2.21 (s, 6H, Me), 1.22 (d, *J* = 6.8 Hz, 12H, Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 152.1, 148.7, 146.3, 135.4, 132.6, 127.1, 118.4, 34.3, 31.1, 29.1, 23.8, 15.8.

**Polycarbonate synthesis (alternate method, CPC2).** **1** (0.9370 g, 3 mmol) and triethylamine (47 μL, 0.3 mmol) were added to an aqueous NaOH solution (0.30 g, 7.5 mmol in 4 mL). A solution of triphosgene (0.367 g, 1.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was then added to the NaOH solution dropwise via syringe. The reaction mixture was vigorously stirred for 10 min and then transferred to a separatory funnel. The organic layer was washed 4 times with water and the organic layer was then poured into ca. 100 mL of rapidly stirring methanol. A white solid precipitated out and was collected on a Buchner funnel. The solid was then washed with methanol and water and dried on the filter for 30 min. The solid was further dried in a vacuum oven overnight to yield 0.69 g of white powder that was spectroscopically identical to **CPC1**.

**Network formation.** **CarvCy** was further purified by dissolution in dichloromethane, followed by passage through a W-Prep2XY Yamazen flash chromatography column, and removal of the solvent

under reduced pressure. Purified **CarvCy** was then heated to approximately 135 °C and poured into a silicone rubber mold having a disc-shaped cavity and cured under flowing nitrogen at 150 °C for 1 h and 210 °C for 24 h using a ramp rate of 5 °C/min, then cooled and de-molded. The resulting pale orange disc was 12 mm in diameter and 4 mm thick. The density of the disc was 1.06 g/mL.

**Water immersion testing.** Cured discs were dried to a  $\pm 0.0001$  g constant weight in a vacuum dessicator, then weighed and immersed in approximately 250 mL de-ionized water maintained at 85 °C for 96 hours. After removal from the water, samples were patted dry and weighed to determine the moisture uptake (on a dry weight basis). These samples were used for wet  $T_g$  determinations

#### **Network Characterization Techniques**

**Differential Scanning Calorimetry (DSC).** 5-10 mg pieces of the cured resin were hermetically sealed in aluminum DSC pans. Samples were then ramped under 50 mL/min of flowing nitrogen at 10 °C/min, first heating to 350 °C, cooling to 100 °C, then re-heating to 350 °C, using a TA Instruments Q200 differential scanning calorimeter.

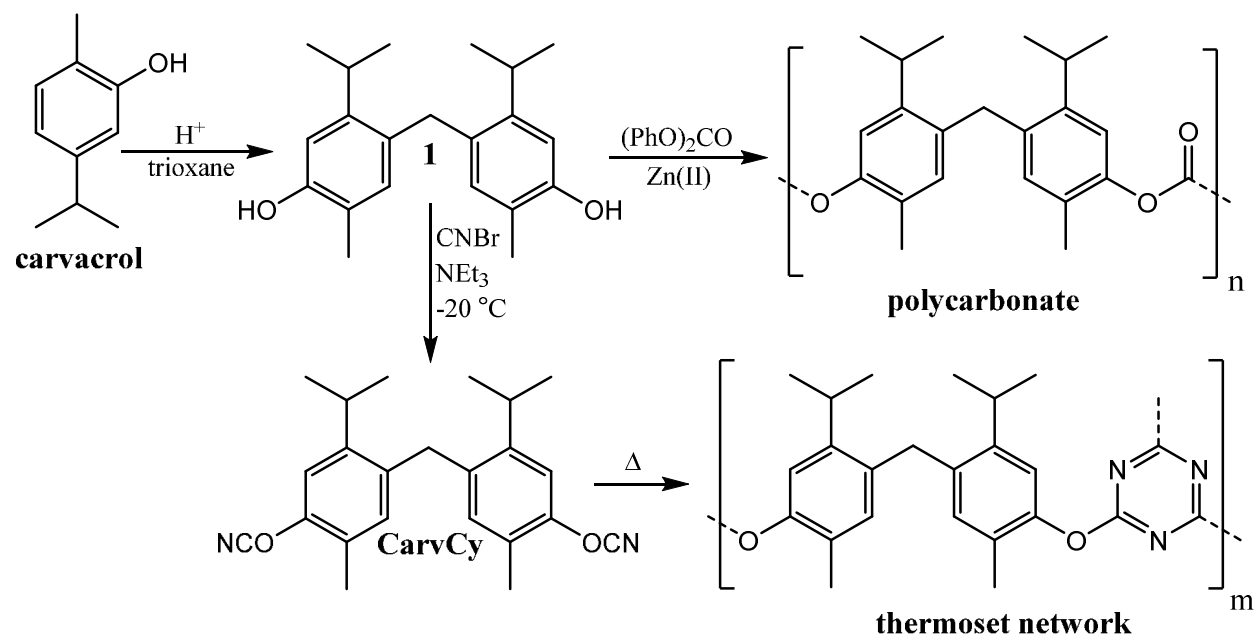
**Oscillatory Thermomechanical Analysis (OTMA).** Cured discs were tested via OTMA with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were initially held in place with a compressive force of 0.2 N using the standard ~5 mm diameter flat cylindrical probe. The force was then modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean force of 0.1 N) and the temperature was ramped twice (heating and cooling) between -50 °C and 200 °C (to aid in determination of thermal lag) followed by heating to 350 °C, cooling to 100 °C, and re-heating to 350 °C, all at 50 °C/min. For samples previously exposed to hot water, the heating rate was decreased to 20 °C/min and the order of segments was: heating to 350 °C, cooling to 100 °C, two cycles between 100 °C and 200 °C for thermal lag determination, and finally heating to 350 °C.



**Thermogravimetric Analysis (TGA).** Samples were heated to 600 °C at 10 °C / min in a TA Instruments Q500 TGA under dry nitrogen or air flowing at 25 mL/min, with the counterweight chamber purged with 10 mL/min dry nitrogen.

## Results and Discussion

A methylene-bridged bisphenol was readily synthesized by reaction of carvacrol with 1,3,5-trioxane in dilute HCl at elevated temperature (Scheme 2). The resulting bisphenol (**1**) precipitated as a solid block which allowed for separation from the reaction medium by simple decantation. The bisphenol was then purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>. Only the para,para-isomer was observed suggesting that the steric hindrance of the alkyl groups plays a significant role in directing the formaldehyde coupling. This selectivity provides an advantage compared to the synthesis of bisphenol A which requires a high phenol:acetone ratio to achieve a high conversion to the *p,p*-isomer.<sup>35</sup> The excess phenol used in the coupling reaction must be removed by vacuum distillation, further increasing the energy demands of the



Scheme 2. Synthesis of a bisphenol, cyanate ester, and polycarbonate from carvacrol

synthesis. **1** has previously been prepared by reaction of carvacrol with formaldehyde under basic conditions, but the reported yield was only 10%.<sup>36</sup> Under the current reaction conditions, high purity bisphenol was isolated in yields of 55% without optimization. A bis(cyanate)ester (**CarvCy**) was then synthesized by reaction of **1** with CNBr in acetone at low temperature. After a water workup and removal of the solvent under reduced pressure, the product spontaneously crystallized to provide an analytically pure sample. The cyanate ester was then characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and X-ray crystallography (Figure 1). The NMR spectra can be found in the supporting information, while the key X-ray data can be found in Table 1. **CarvCy** crystallized in the P 1 21/c 1 space group with one independent molecule in the asymmetric unit and four molecules in the unit cell. The aromatic rings are oriented at 77.4° to each other and no significant pi-stacking interactions were observed. Short non-bonded contacts [3.169 (2) Å] exist between carbon and nitrogen atoms in cyanate ester

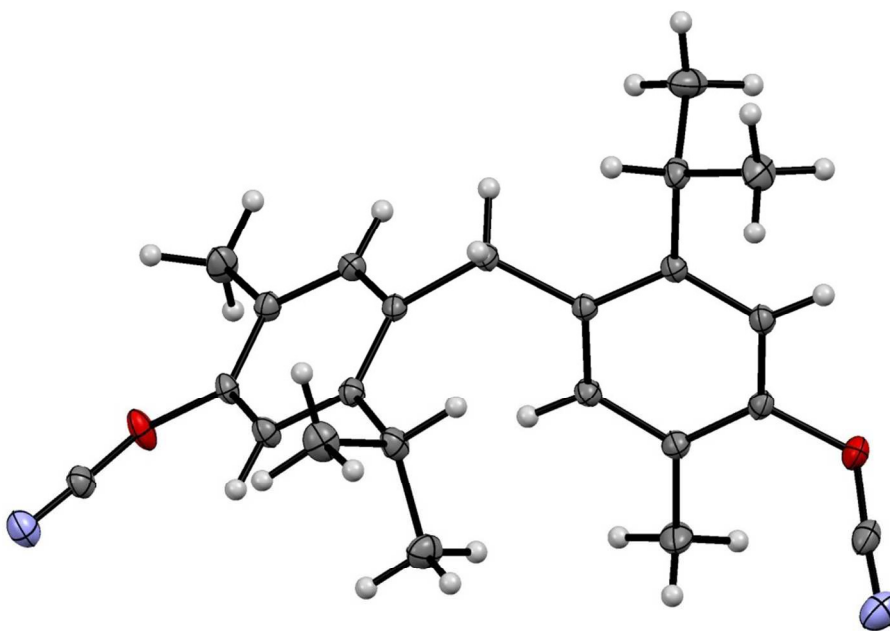


Figure 1. Solid state structure of **CarvCy**. Thermal ellipsoids are displayed at the 50% probability level

**Table 1. X-ray Crystallographic Data for 2**

empirical formula	C <sub>23</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub>
formula weight	362.46
temperature	100(2) K
wavelength	0.71073 Å
crystal size	0.177 x 0.225 x 0.334 mm
crystal system	monoclinic
space group	P 1 21/c 1
unit cell dimensions	a = 9.0471(6) Å, α = 90° b = 17.5709(11) Å, β = 109.2500(10)° c = 12.9430(8) Å, γ = 90°
volume	1942.5(2) Å <sup>3</sup>
Z	4
density (calculated)	1.239 g/cm <sup>3</sup>
θ range for data collection	2.03 to 32.67°
reflections collected	35839
independent reflections	7077 [R(int) = 0.0358]
data / restraints / parameters	7077 / 0 / 250
goodness-of-fit on F <sup>2</sup>	1.035
final R indices [I > 2σ(I)]	R1 = 0.0495, wR2 = 0.1262

groups of neighboring molecules in the crystal lattice (Figure 2). These non-bonded contacts are shorter than the sum of the van der Waals radii (3.25 Å) and suggest that interactions between the cyanate groups strongly influence the lattice formation. A similar effect has been observed in the solid state structure of the bis(cyanate) ester derived from bisphenol A (BADCy) which exhibited intermolecular C-N contacts of 3.484(4) Å, N-N contacts of 3.546(6) Å, and N-O contacts of 3.318 (4) Å.<sup>37</sup> In both examples, the cyanate ester is pre-oriented in the solid state for formation of a cross-linked network structure. Although the crystalline order of the material is lost upon melting, it is likely that the interaction between the cyanate ester groups is also important in the melt and contributes to effective cyclotrimerization.

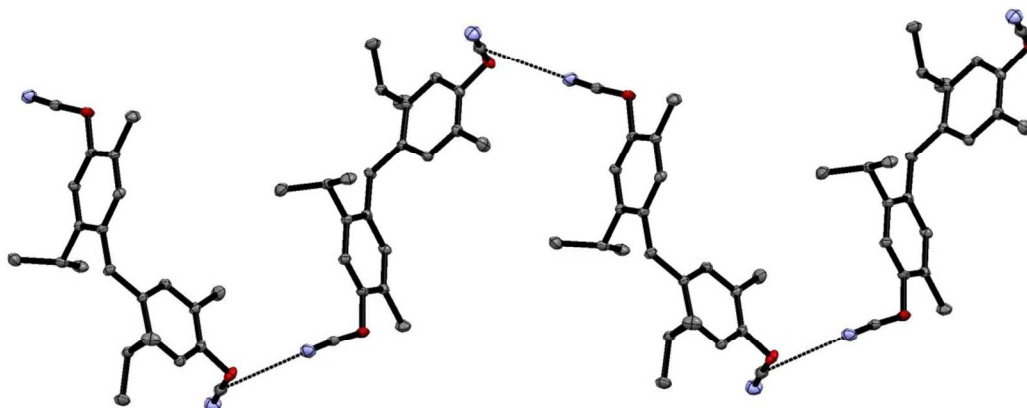


Figure 2. X-ray structure of **CarvCy** showing the short non-bonded contacts between molecules in the solid state. Hydrogen atoms have been omitted for clarity.

After characterizing the cyanate ester monomer, the cure chemistry of the resin was first probed by DSC (Figure 3). The resin melted cleanly at 117 °C with onset of cure observed at 194 °C. The enthalpy change attributed to cyclotrimerization was 112 kJ/(mol -OCN), consistent with complete cure.<sup>38</sup> The

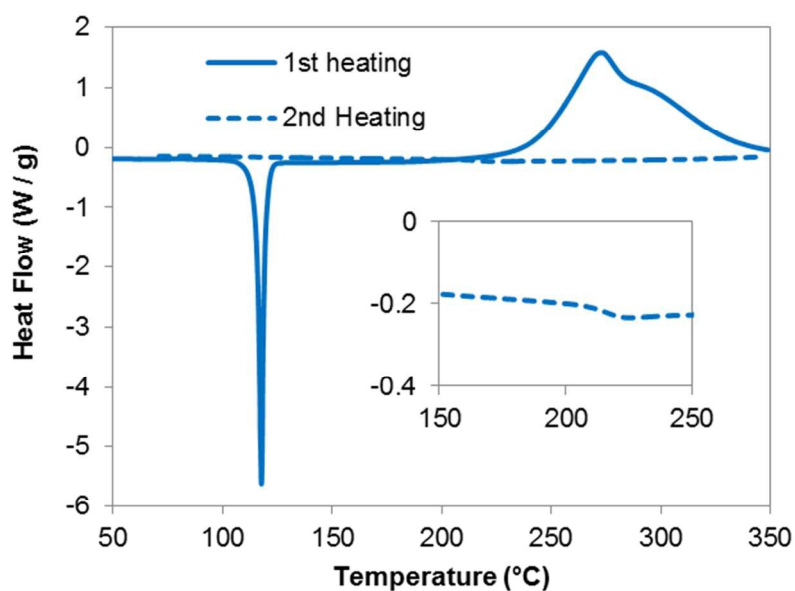


Figure 3. DSC data for **CarvCy**

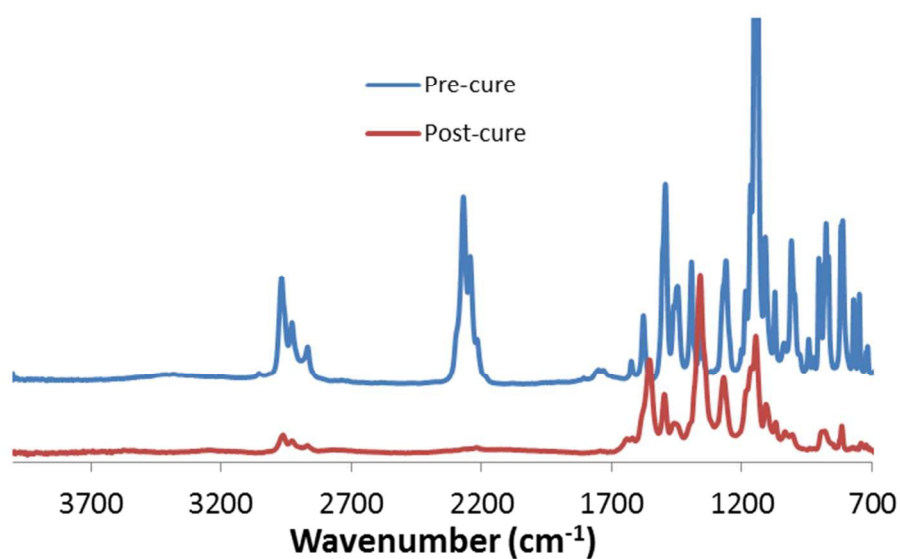


Figure 4. FTIR data for CarvCy before and after cure

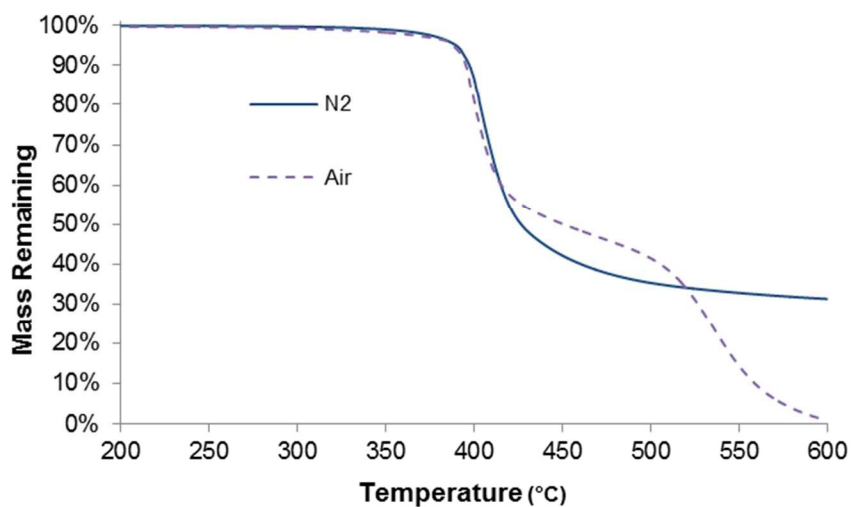


Figure 5. TGA data for cured CarvCy

DSC curve obtained after cure of the resin indicates a conversion of about 97%. Similarly, IR spectra taken before and after the cure reaction showed complete elimination of the C-N stretching frequency

at about  $2250\text{ cm}^{-1}$ , confirming the high degree of cure (Figure 4). The thermal properties of the cured resin were then evaluated by TGA (Figure 5). The material showed excellent thermal stability, particularly given the number of aliphatic groups present in the parent molecule. 5% weight loss was observed at 390 and 388 °C under  $\text{N}_2$  and air, respectively. The char yield at 600 °C in nitrogen was 31%, while the char yield in air was less than 1%. The significant discrepancy between air and nitrogen suggests that the aliphatic groups are particularly sensitive to oxidative degradation. These results are similar to other cyanate esters with increased aliphatic content including a cyanate ester resin bridged by dipentene,<sup>39</sup> and a bis(cyanate) ester derived from eugenol.<sup>5,6</sup> In contrast, the commercial cyanate ester resins **BADCy** and tetramethyl bisphenol F cyanate ester (**AroCy M-10**) both exhibit 5% weight loss in nitrogen at 443 °C<sup>40</sup> and have char yields in  $\text{N}_2$  of 39 and 41%, respectively. Given that **AroCy M-10** has two methyl groups on each aromatic ring but has a similar degradation onset temperature to **BADCy**, it seems likely that the lower thermal stability of **CarvCy** is due to the isopropyl substituents.

The  $T_g$  of cured **CarvCy** was obtained via thermomechanical analysis (Figure 6) and determined to be 224 °C (loss peak). To evaluate the performance of the resin under hot/wet conditions, a cured sample

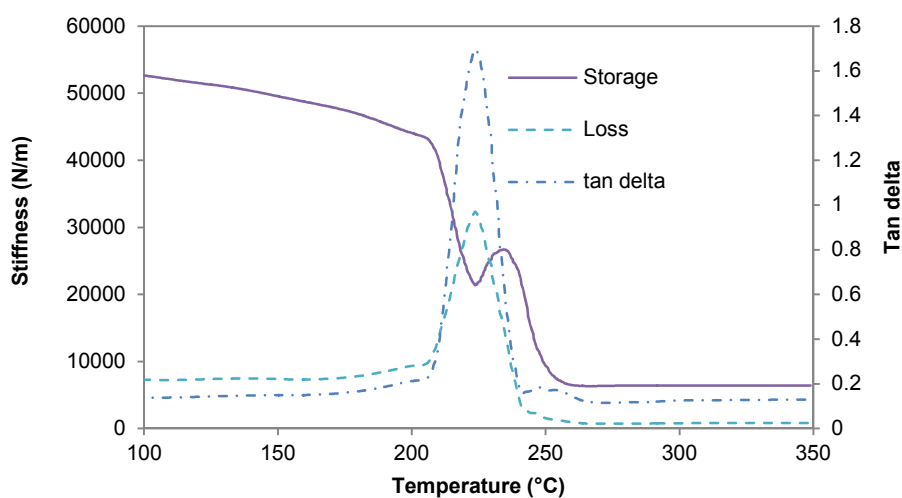


Figure 6. TMA data for cured **CarvCy**

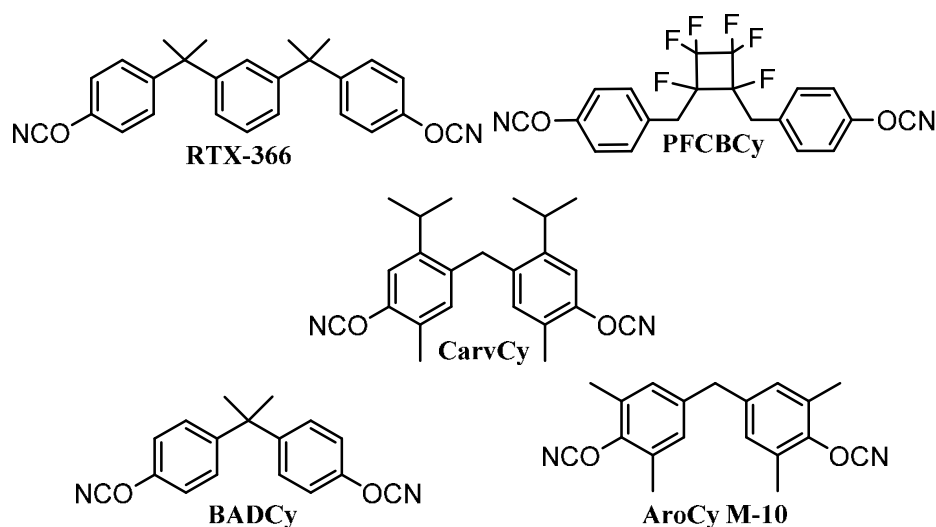


Figure 7. Structures of cyanate esters discussed in this work.

was placed in 85 °C water for 4 days and exhibited water uptake of only 0.7%. This is one of the lowest water uptakes measured for any cyanate ester, roughly 50% that of **BADCy**<sup>13</sup> and similar to that of **RTX-366** (0.6-0.7%)<sup>41</sup> and a recently reported cyanate ester prepared from bisphenol T [**PFCBCy**, 0.56 (10)%].<sup>42</sup> The structures of **RTX-366** and **PFCBCy** can be found in Figure 7. **RTX-366** has a fully cured  $T_g$  (uncatalyzed) of 204 °C,<sup>40</sup> while **PFCBCy** has a fully cured  $T_g$  of 190 °C.<sup>42</sup> By comparison, **CarvCy** has a  $T_g$  20-35 °C higher and outperforms both of these previous resins when water uptake and glass transition temperature are considered in concert. To further evaluate the behavior of **CarvCy** in humid environments, a wet  $T_g$  was determined using a resin disk subjected to the hot water treatment (Figure S6). The wet  $T_g$  (221 °C) was only three degrees lower than the dry  $T_g$ , showing that the cured resin was virtually unaffected by the water exposure at elevated temperature. The wet  $T_g$  knockdown was lower than that observed with **AroCy M-10** (8 °C)<sup>43</sup> and significantly lower compared to **BADCy** which has a reported wet  $T_g$  knockdown of 57 °C.<sup>43</sup> Previous work by Shimp<sup>44</sup> and a recent paper by Guenther et al.<sup>45</sup> has shown that having a methyl group *ortho* to the cyanate ester group can lead to decreased water uptake. Similarly, the combination of the *ortho*-methyl groups and the hydrophobic isopropyl groups in the position *meta* to the cyanate ester group impart excellent water resistance to **CarvCy**.

After evaluating the properties of **CarvCy** it was of interest to synthesize a polycarbonate from the bisphenol. Reaction of **1** with diphenyl carbonate in the presence of zinc acetate resulted in a  $\text{CH}_2\text{Cl}_2$  soluble polycarbonate (**CPC1**) with  $M_n = 5519$  daltons and  $M_w/M_n = 3.06$ . The polymer was then analyzed via DSC and a glass transition temperature of  $113\text{ }^\circ\text{C}$  was observed. This value is about  $15\text{ }^\circ\text{C}$  lower than that of a bisphenol-A derived polycarbonate of similar molecular weight.<sup>46,47</sup> TGA showed 5% weight loss at  $353\text{ }^\circ\text{C}$  under nitrogen and  $342\text{ }^\circ\text{C}$  in air (Figure 8). The char yield was 19.8% under nitrogen and only 1.5% in air. These results are similar to those observed for **CarvCy**, while the char yield in nitrogen is about 10% less than that observed for bisphenol A polycarbonate.<sup>48</sup> No melting point was observed in the DSC up to  $250\text{ }^\circ\text{C}$ . A higher molecular weight polycarbonate was then synthesized

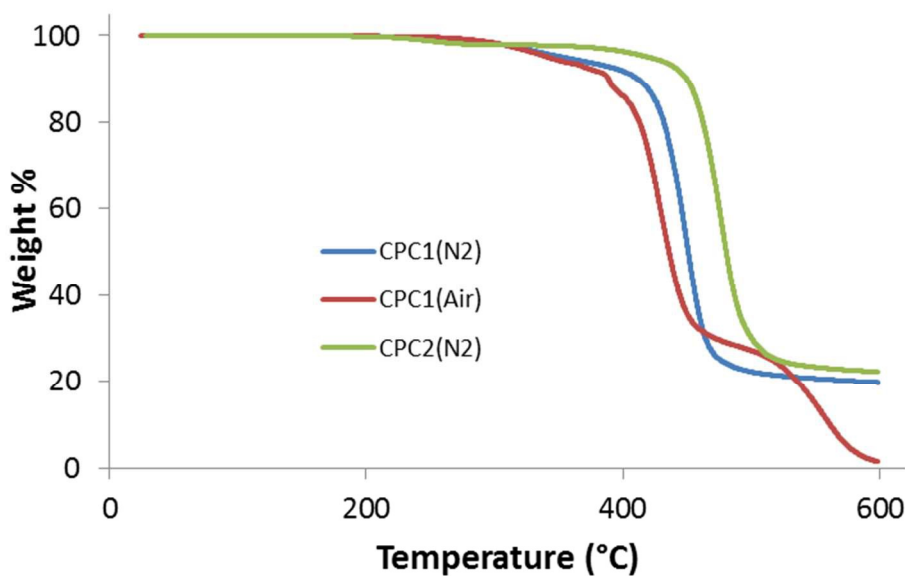


Figure 8. TGA data for the polycarbonate in air and nitrogen



by interfacial polymerization with triphosgene.<sup>49</sup> This procedure resulted in a CH<sub>2</sub>Cl<sub>2</sub> soluble polycarbonate (**CPC2**) with  $M_n = 10,200$  and  $M_w/M_n = 1.60$ . The  $T_g$  increased slightly to 119 °C, approximately 20 °C lower than a BPA polycarbonate of equivalent molecular weight.<sup>46,47</sup> The minor change observed in  $T_g$  for **CPC2** despite nearly doubling the molecular weight of **CPC1** suggests that 120°C is near the maximum  $T_g$  for this class of polycarbonate, regardless of molecular weight. **CPC2** exhibited higher thermal stability than **CPC1** with 5% weight loss at 421 °C in nitrogen and a char yield of 22%. Given the higher molecular weight and lower PDI of **CPC2**, the lower thermal stability of **CPC1** is likely due to a higher concentration of low molecular weight oligomers. Despite the presence of isopropyl groups on the aromatic rings, **CPC2** exhibited 5% weight loss at a temperature only 24 °C lower than BPA polycarbonate (445 °C)<sup>50</sup> and in comparison to some recently described bio-based polycarbonates, **CPC2** exhibits significantly higher thermal stability. For example, the 5% loss temperature of **CPC2** is more than 120 °C higher than that observed for polycarbonates derived from camphorquinone<sup>51</sup> and about 80 °C higher than isosorbide derived polycarbonates.<sup>52-54</sup> In comparison to bio-based polycarbonates derived from aromatic compounds, **CPC2** exhibited 5% weight loss at a temperature about 30 °C higher than a creosol-derived polycarbonate,<sup>49</sup> more than 110 °C higher than a polycarbonate derived from eugenol,<sup>5</sup> and 130 °C higher than a polycarbonate derived from vanillin.<sup>4</sup>

## Conclusions

Carvacrol and the derivative bisphenol 4,4'-methylenebis(5-isopropyl-2-methylphenol) are sustainable and versatile starting materials for the synthesis of high performance thermosetting and thermoplastic resins. The synthesis of carvacrol from abundant terpenoids and lignocellulosic sources may allow for the bisphenol and derivative polymers to be produced on an industrially relevant scale. Although a cyanate ester resin and polycarbonate were targeted in the current research, the bisphenol could be readily utilized as a precursor to a variety of polymers including epoxy resins, phthalonitrile resins, and

polyether ether ketones. As in the case of other renewable phenols, the unique functionality of carvacrol compared to simple phenol allows for intriguing properties. In particular, the aliphatic substituents greatly reduce the water uptake of the cyanate ester resin, while maintaining an acceptable glass transition temperature and good thermal stability. The results of the current study highlight the ability of sustainable phenols to impart unique performance characteristics to derivative polymers that in some cases are superior to those of conventional petroleum-based resins.

### **Acknowledgements**

The authors would like to thank The Strategic Environmental Research and Development Program (SERDP WP-2214) and the Air Force Office of Scientific Research for financial support of this work. NREIP fellowships funded by the Office of Naval Research for TAK and PJS are also gratefully acknowledged. The authors would further like to thank Dr. Lee Cambrea, Dr. Matthew Davis, and Dr. William Lai for their valuable contributions to this work.

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