Electronic Supplementary Information (ESI)

High $T_g$ thermosetting resins from resveratrol

Jessica J. Cash, Matthew C. Davis,* Michael D. Ford, Thomas J. Groshens, Andrew J. Guenthner,*
Benjamin G. Harvey, Kevin R. Lamison, Joseph M. Mabry, Heather A. Meylemans, Josiah T. Reams, and Christopher M. Sahagun

Chemistry & Materials Division, Michelson Laboratory, Naval Air Warfare Center, China Lake, California, 93555, USA
Air Force Research Laboratory, Aerospace Systems Directorate Edwards AFB, California, 93524, USA

Electronic Supplementary Information (ESI) Available:

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General Consideration and Instrumentation

The melting points were collected on a Mel-Temp II from Laboratory Devices (Holliston, MA) and are not corrected. All NMR data were collected on a Bruker Avance II 300 MHz spectrometer ($^1$H at 300 MHz, $^{13}$C at 75 MHz). Nuclear magnetic resonance data (free-induction decays) were processed using NUTS software from Acorn NMR (Livermore, CA). Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS) or residual proton in the specified solvent. Coupling constants ($J$) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.

Resveratrol is commercially available, cyanogen bromide (BrCN), 5% palladium on carbon, triethylamine (TEA) and all other reagents and solvents were purchased from Sigma-Aldrich (Milwaukee). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

**CAUTION!** The procedures involving BrCN are hazardous due to toxicity of this reagent. Although BrCN is a solid, it has a very high vapor pressure at room temperature. Reactions involving this reagent must be carried out inside a well-ventilated fume cupboard.

Monomer Synthesis

3,4',5-Trihydroxydibenzyl (dihydroresveratrol)

Resveratrol (10 g, 44 mmol) was dissolved in THF (500 mL) and 5% Pd/carbon catalyst (1 g) was added. The mixture was reduced under H$_2$ atmosphere (25 torr). The catalyst was filtered and the solvent was rotary evaporated leaving an off-white solid (9.9 g).

Yield: 98%.

Mp 159–161 °C (from toluene/EtOAc) (lit., 156–157 °C).

Found: C, 73.17; H, 6.14. C$_{14}$H$_{14}$O$_3$ requires C, 73.03; H, 6.13%.

$\delta_H$ (300 MHz; CDCl$_3$/DMSO; Me$_4$Si): 8.39 (1 H, s, 4'-OH), 8.34 (2 H, s, 3,5'-OH), 6.99 (2 H, d, $J$ = 8, 2'-H and 6'-H), 6.74 (2 H, d, $J$ = 8, 3'-H and 5'-H), 6.23–6.18 (3 H, m, 2-H and 4-H and 6-H), 2.8–2.62 (4 H, m, both CH$_2$).

$\delta_C$ (100 MHz; CDCl$_3$/DMSO): 157.95, 155.00, 144.40, 132.95, 129.32, 115.38, 107.34, 100.75, 38.21, 36.67.

**E 3,4',5-tricyanostilbene** (resveratrol tricyanate, 1)

A round-bottomed flask (500 mL) equipped with magnetic stirring bar was charged with resveratrol (2.5 g, 11 mmol), BrCN (4.66 g, 44 mmol, 4 equiv) and 200 mL anhydrous acetone. The mixture was stirred in a -20 °C bath before TEA (3.55 g, 35 mmol, 3.2 equiv) was added dropwise. After stirring 2 h, the reaction mixture was diluted with H$_2$O (200 mL). The crude white product was collected on a medium porosity glass frit and dried under vacuum. Recrystallization gave the title compound (2.7 g) as colorless needles.

Yield: 81%.

Mp 161–163 °C (from isopropanol/MeCN).
Found: C, 67.33; H, 2.86; N, 13.92. C_{17}H_{11}N_{3}O_{3} requires C, 67.33; H, 2.99; N, 13.86%.

δ_H (300 MHz; CDCl_3; Me_4Si): 7.63 (2 H, d, J = 8, 3′-H and 5′-H), 7.44 (2 H, d, J = 2, 4′-H), 7.36 (2 H, d, J = 8, 2′-H and 6′-H), 7.22 (1 H, d, J_{AB} = 16, alkene), 7.14 (1 H, t, J = 2, 2-H and 6-H), 7.05 (1 H, d, J_{AB} = 16, alkene).

δ_C (100 MHz; CDCl_3): 153.93, 153.21, 142.41, 134.71, 132.17, 129.27, 126.34, 116.26, 111.33, 108.59, 107.72, 103.29.

3,4′,5-Tricyanatodibenzyl
(dihydroresveratrol tricyanate, 2)

A procedure analogous to that of the synthesis of resveratrol tricyanate was employed. Dihydroresveratrol (2.79 g, 12 mmol), BrCN (48 mmol, 4 equiv), TEA (3.91 g, 39 mmol, 3.2 equiv) and acetone (200 mL) gave the product (2.3 g).

Yield: 62%.

Mp 118–120 °C (from heptanes/EtOAc).

Found: C, 66.86; H, 3.55; N, 13.66. C_{17}H_{11}N_{3}O_{3} requires C, 66.88; H, 3.63; N, 13.76%.

δ_H (300 MHz; DMSO; Me_4Si): 7.47–7.39 (5 H, m), 7.39–7.33 (2 H, m), 3.04 (2 H, m, CH_2), 2.94 (2 H, m, CH_2).

δ_C (100 MHz; DMSO): 152.67, 151.03, 147.51, 139.84, 130.75, 115.35, 114.31, 108.82, 107.92, 102.68, 36.18, 35.23.

References


NMR Spectra

Figure S1. $^1$H NMR spectrum of 3,4',5-trihydroxydibenzyl (dihydroesveratrol)
Figure S2. $^{13}$C NMR spectrum of 3,4',5'-trihydroxydibenzyl (dihydroresveratrol)
Figure S3. $^1$H NMR spectrum of trans 3,4',5-tricyanostilbene (resveratrol tricyanate, 1)
Figure S4. $^{13}$C NMR spectrum of trans 3,4',5-tricyanostilbene (resveratrol tricyanate, 1)
Figure S5. $^1$H NMR spectrum of 3,4',5-Tricyanatodibenzyl (dihydroresveratrol tricyanate, 2)
Figure S6. $^{13}$C NMR spectrum of 3,4',5-Tricyanatodibenzyl (dihydroresveratrol tricyanate, 2)
X-ray crystallography

Crystallographic data (without structure factors) for 1 (CCDC 777073) and 2 (CCDC 804881) have been deposited with Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Figure S7. X-ray crystal structure of Trans 3,4',5-tricyanostilbene (resveratrol tricyanate, 1), thermal ellipsoids at 50 % probability.
Figure S8. X-ray crystal structure of \textbf{3,4',5-Tricyanodibenzyl} (dihydroporesseratrol tricyanate, 2), thermal ellipsoids at 50% probability.
Thermal analysis of polycyanurates

Figure S9. DSC trace of monomer 1; the “L”-shaped feature on the high-temperature side of the exotherm indicates incomplete cure due to vitrification.
Figure S10. DSC trace of monomer 2; the gradual drift of the signal toward the baseline after the exotherm, along with the reduced asymmetry of the exotherm, indicate a higher degree of conversion was achieved compared to monomer 1.

Figure S11. FT-IR spectra of monomer 2 cured at 250 °C for various times. After 60 min, the sample has reached a constant conversion; the modest peaks near 2250 cm\(^{-1}\) indicate significant concentration of cyanate ester remain; the large peak at 1565 cm\(^{-1}\) is associated with triazine ring.
Table S1. Summary of oscillatory TMA data

<table>
<thead>
<tr>
<th>Polycyanurates</th>
<th>Run Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>$T_g$ (Loss peak, °C)</td>
<td>CTE$^a$ @ 150 °C (ppm/°C)</td>
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<tr>
<td>270</td>
<td>57</td>
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<tr>
<td>278</td>
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<tr>
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<td>58</td>
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</tr>
<tr>
<td>179</td>
<td>NM</td>
</tr>
</tbody>
</table>

$^a$ Coefficient of thermal expansion. $^b$ Primary peak. $^c$ The reliability of CTE data from wet samples is not well-established, however this value appears reasonable.

Figure S11. TGA data for polycyanurate 1.
Figure S12. TGA data for polycyanurate 2.