Supporting Information For

Renewable Thermosetting Resins and Thermoplastics from Vanillin

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Contents

X-ray data collection for compound 6. A specimen of **6**, with approximate dimensions 0.092 mm x 0.138 mm x 0.272 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 12.20 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 8100 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 1354 were independent (average redundancy 5.982, completeness = 100.1%, R_{int} = 2.86%) and 966 (71.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 3.8765(4) Å, b = 12.2303(13) Å, c = 16.1995(18) Å, β = 95.9060(17)°, volume = 763.95(14) $Å^3$, are based upon the refinement of the XYZ-centroids of 1817 reflections above 20 σ(I) with 5.056° < 2θ < 48.36°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.920. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9910.

The final anisotropic full-matrix least-squares refinement on F^2 with 126 variables converged at R1 = 4.06%, for the observed data and wR2 = 10.69% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.265 $e^-/Å^3$ and the largest hole was -0.166 $e^-/Å^3$ with an RMS deviation of 0.031 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.401 g/cm^3 and F(000), 336 e^-.

Table S1. Sample and crystal data for 6

Chemical formula	$C_{18}H_{14}N_2O_4$	
Formula weight	322.31	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.092 x 0.138 x 0.272 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 3.8765(4) Å	α = 90°
	b = 12.2303(13) Å	β = 95.9060(17)°
	c = 16.1995(18) Å	γ = 90°
Volume	763.95(14) $Å^3$	
Z	2	
Density (calculated)	1.401 g/cm^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	336	

Table S2. Data collection and structure refinement for 6.

Theta range for data collection	2.09 to 25.00°

Index ranges	-4<=h<=4, -14<=k<=14, -19<=l<=19
Reflections collected	8100
Independent reflections	1354 [R(int) = 0.0286]
Coverage of independent reflections	100.1%
Absorption correction	multi-scan
Max. and min. transmission	0.9910 and 0.9730
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1354 / 0 / 126
Goodness-of-fit on F^2	1.033
Final R indices	966 data; $I>2\sigma(I)$ R1 = 0.0406, wR2 = 0.0908
	all data R1 = 0.0635, wR2 = 0.1069
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0393P)^2+0.2954P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.265 and -0.166 eÅ^{-3}
R.M.S. deviation from mean	0.031 eÅ^{-3}

Table S3. Bond lengths (Å) for 6

O1-C8	1.286(2)	O1-C4	1.428(2)
O2-C5	1.362(2)	O2-C9	1.427(2)
C1-C2	1.379(3)	C1-C6	1.393(3)
C1-C7	1.473(3)	C2-C3	1.376(3)
C2-H1	0.99(2)	C3-C4	1.363(3)
C3-H2	0.97(2)	C4-C5	1.385(2)
C5-C6	1.387(3)	C6-H3	0.921(19)
N1-C8	1.134(3)	C7-C7	1.298(4)
C7-H4	0.98(3)	C9-H9A	0.96
C9-H9B	0.96	C9-H9C	0.96

Table S4. Bond angles (°) for 6

C8-O1-C4	117.22(16)	C5-O2-C9	117.18(16)
C2-C1-C6	118.64(18)	C2-C1-C7	118.33(19)
C6-C1-C7	123.02(19)	C3-C2-C1	121.2(2)
C3-C2-H1	118.7(14)	C1-C2-H1	120.0(14)

C4-C3-C2	118.8(2)	C4-C3-H2	119.2(14)
C2-C3-H2	122.1(14)	C3-C4-C5	122.70(17)
C3-C4-O1	122.43(17)	C5-C4-O1	114.87(17)
O2-C5-C4	115.96(16)	O2-C5-C6	126.61(18)
C4-C5-C6	117.42(18)	C5-C6-C1	121.23(18)
C5-C6-H3	116.9(12)	C1-C6-H3	121.8(12)
C7-C7-C1	127.2(3)	C7-C7-H4	111.5(16)
C1-C7-H4	121.1(16)	N1-C8-O1	175.7(2)
O2-C9-H9A	109.5	O2-C9-H9B	109.5
H9A-C9-H9B	109.5	O2-C9-H9C	109.5
H9A-C9-H9C	109.5	H9B-C9-H9C	109.5

X-ray data collection for compound 7. A specimen of **7**, approximate dimensions 0.070 mm x 0.195 mm x 0.255 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 12.20 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 8545 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 1399 were independent (average redundancy 6.108, completeness = 100.0%, R_{int} = 2.62%, R_{sig} = 1.64%) and 1097 (78.41%) were greater than $2\sigma(F^2)$. The final cell constants of a = 4.4010(3) Å, b = 12.3035(9) Å, c = 14.8314(11) Å, β = 97.5930(10)°, volume = 796.04(10) $Å^3$, are based upon the refinement of the XYZ-centroids of 2135 reflections above 20 σ(I) with 4.317° < 2θ < 48.90°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.942. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9760 and 0.9930.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 2 for the formula unit, $C_{18}H_{16}N_2O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 110 variables converged at R1 = 3.50%, for the observed data and wR2 = 9.62% for all data. The goodness-of-fit was 1.038. The largest peak in the final difference electron density synthesis was 0.115 $e^-/Å^3$ and the largest hole was -0.151 $e^-/Å^3$ with an RMS deviation of 0.029 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.353 g/cm^3 and F(000), 340 e^-.

Table S5. Sample and crystal data for 7

Identification code	Compound **7**	
Chemical formula	$C_{18}H_{16}N_2O_4$	
Formula weight	324.33	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.195 x 0.255 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 4.4010(3) Å	α = 90°
	b = 12.3035(9) Å	β = 97.5930(10)°
	c = 14.8314(11) Å	γ = 90°
Volume	796.04(10) $Å^3$	
Z	2	
Density (calculated)	1.353 g/cm^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	340	

Table S6. Data collection and structure refinement for 7

Theta range for data	2.16 to 25.00°

collection		
Index ranges	-5<=h<=5, -14<=k<=14, -17<=l<=17	
Reflections collected	8545	
Independent reflections	1399 [R(int) = 0.0262]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9930 and 0.9760	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1399 / 0 / 110	
Goodness-of-fit on F^2	1.038	
Final R indices	1097 data; $I>2\sigma(I)$	R1 = 0.0350, wR2 = 0.0863
	all data	R1 = 0.0474, wR2 = 0.0962
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0423P)^2+0.1584P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.115 and -0.151 eÅ^{-3}	
R.M.S. deviation from mean	0.029 eÅ^{-3}	

O2-C9	1.2797(18)	O2-C5	1.4282(16)
O1-C4	1.3596(17)	O1-C8	1.4257(19)
N1-C9	1.127(2)	C5-C6	1.363(2)
C5-C4	1.3838(19)	C4-C3	1.3845(19)
C3-C2	1.389(2)	C3-H3	0.93
C2-C7	1.380(2)	C2-C1	1.5114(19)

Table S7. Bond lengths (Å) for 7

C1-C1	1.518(3)	C1-H1	0.97
C1-H2	0.97	C7-C6	1.388(2)
C7-H5	0.93	C6-H4	0.93
C8-H7	0.96	C8-H8	0.96
C8-H6	0.96		

Table S8. Bond angles (°) for 7

C9-O2-C5	118.70(12)	C4-O1-C8	116.78(12)
N1-C9-O2	175.05(19)	C6-C5-C4	122.89(13)
C6-C5-O2	123.16(13)	C4-C5-O2	113.95(13)
O1-C4-C5	116.35(12)	O1-C4-C3	126.21(13)
C5-C4-C3	117.44(14)	C4-C3-C2	121.37(13)
C4-C3-H3	119.3	C2-C3-H3	119.3
C7-C2-C3	118.98(13)	C7-C2-C1	121.60(14)
C3-C2-C1	119.40(13)	C2-C1-C1	112.95(15)
C2-C1-H1	109.0	C1-C1-H1	109.0
C2-C1-H2	109.0	C1-C1-H2	109.0
H1-C1-H2	107.8	C2-C7-C6	120.80(14)
C2-C7-H5	119.6	C6-C7-H5	119.6
C5-C6-C7	118.52(14)	C5-C6-H4	120.7
C7-C6-H4	120.7	O1-C8-H7	109.5
O1-C8-H8	109.5	H7-C8-H8	109.5
O1-C8-H6	109.5	H7-C8-H6	109.5
H8-C8-H6	109.5		

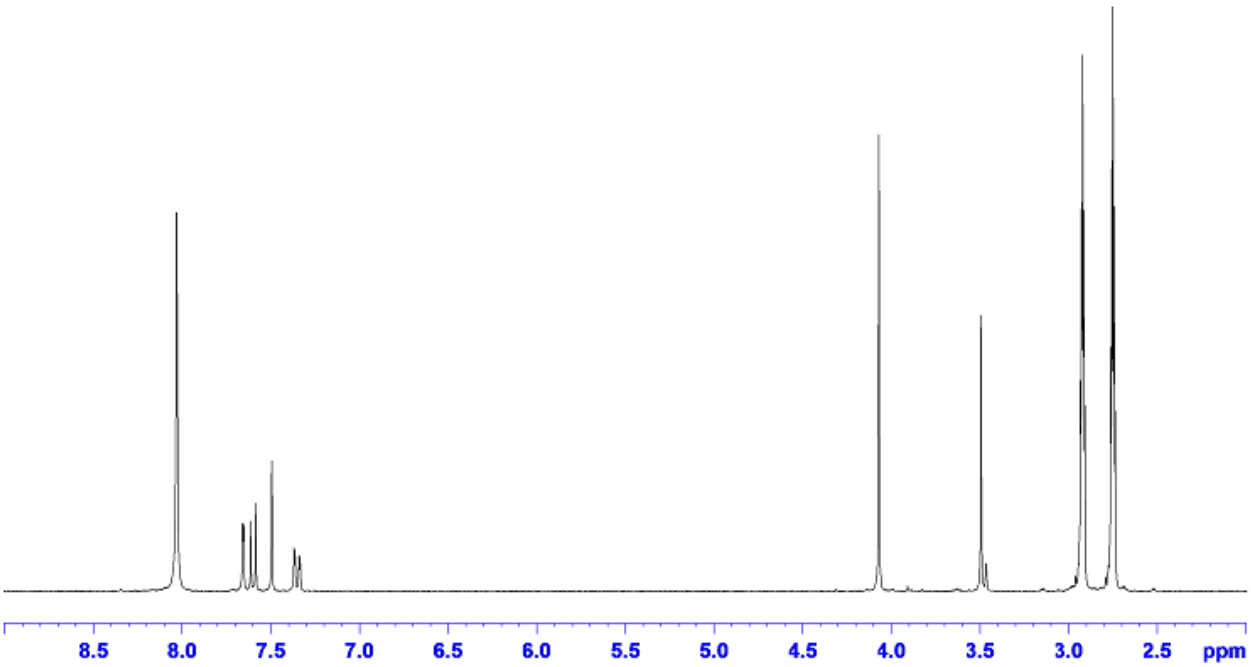

Figure S1. ^{1}H NMR spectrum of compound 6 in DMF-d_7

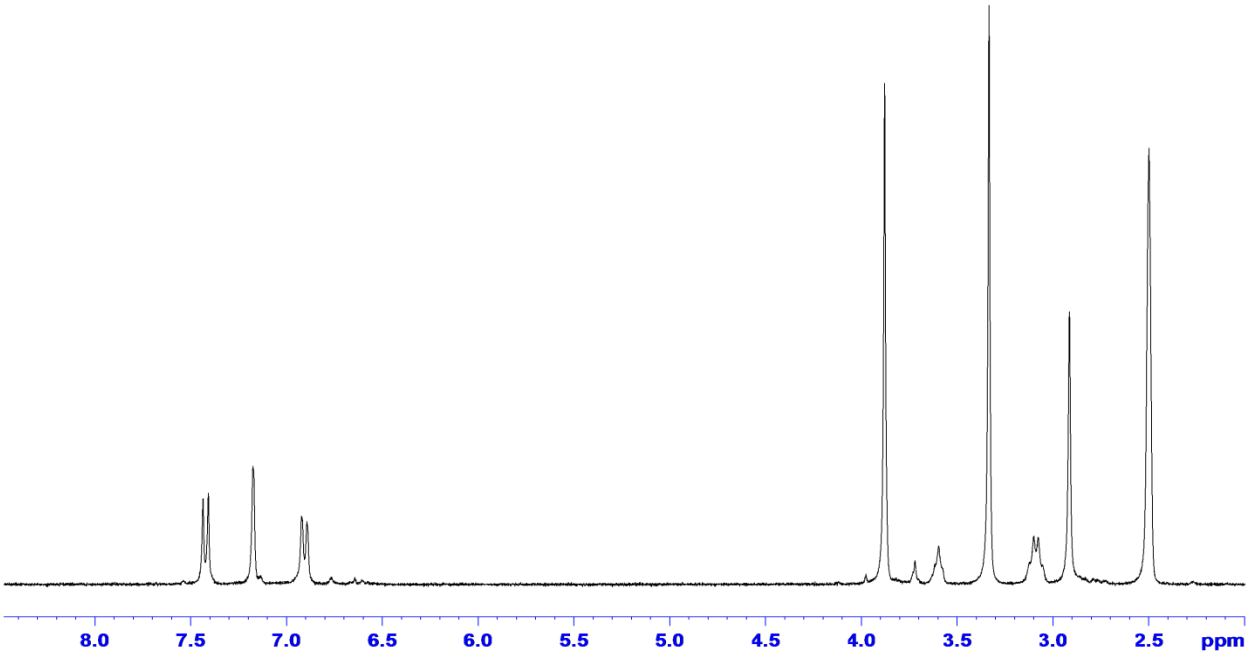

Figure S2. ^{1}H NMR spectrum of compound **7** in DMSO-d_6. Due to the very low solubility of compound **7** in common organic solvents including DMSO, the resonances due to impurities are highly exaggerated. For example, THF can be observed at ~3.6 ppm, water (from the NMR solvent) at ~3.3 ppm, and triethylamine hydrochloride at ~3.2 ppm

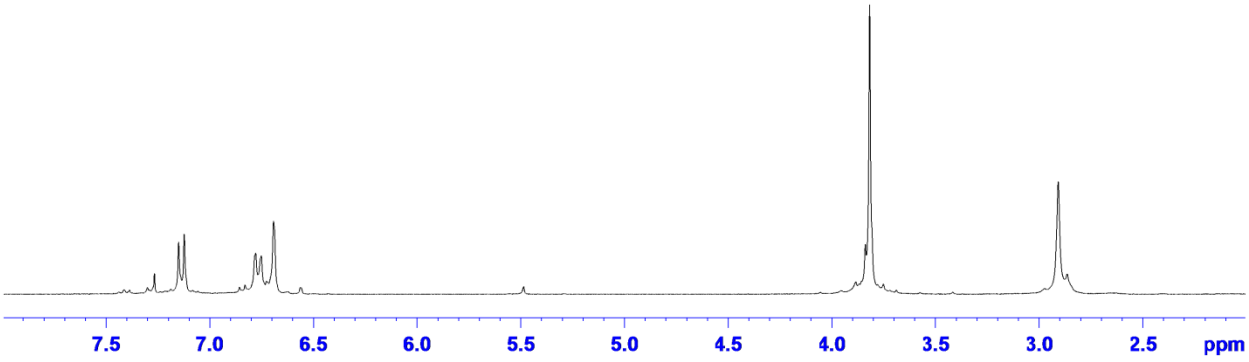

Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of the polycarbonate derived from compound **5**

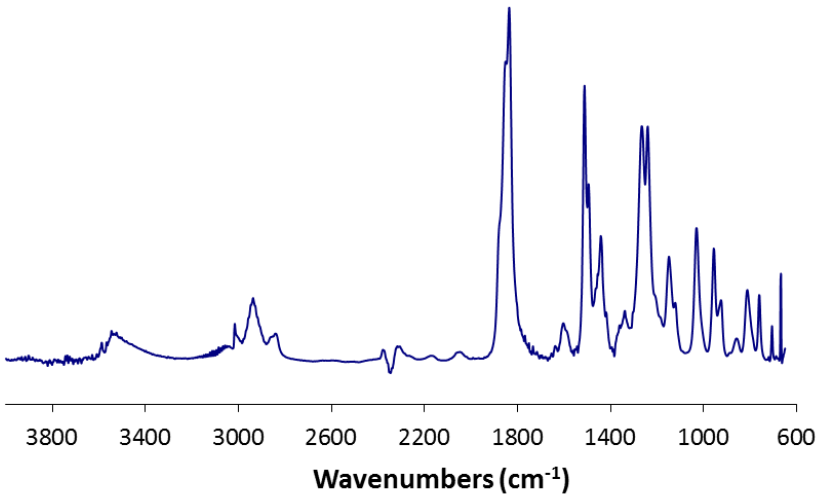

Figure S4. Gas phase IR data of polycarbonate decomposition products