Supporting Information for

**Degradability, Thermal Stability, and High Thermal Transitions in Spiro Polycycloacetals
Partially Derived from Lignin**

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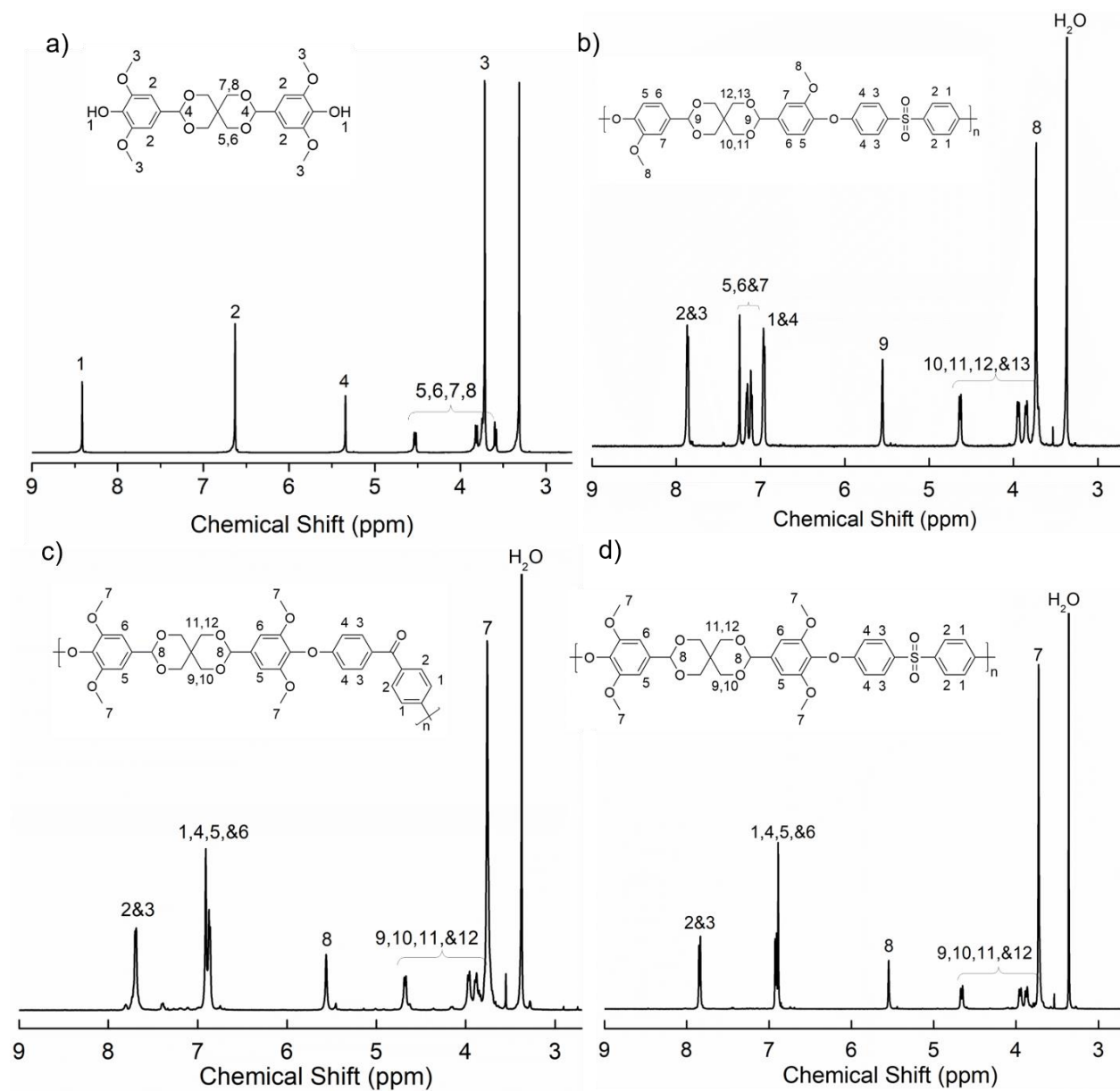mlrobertson@uh.edu
713-743-2748

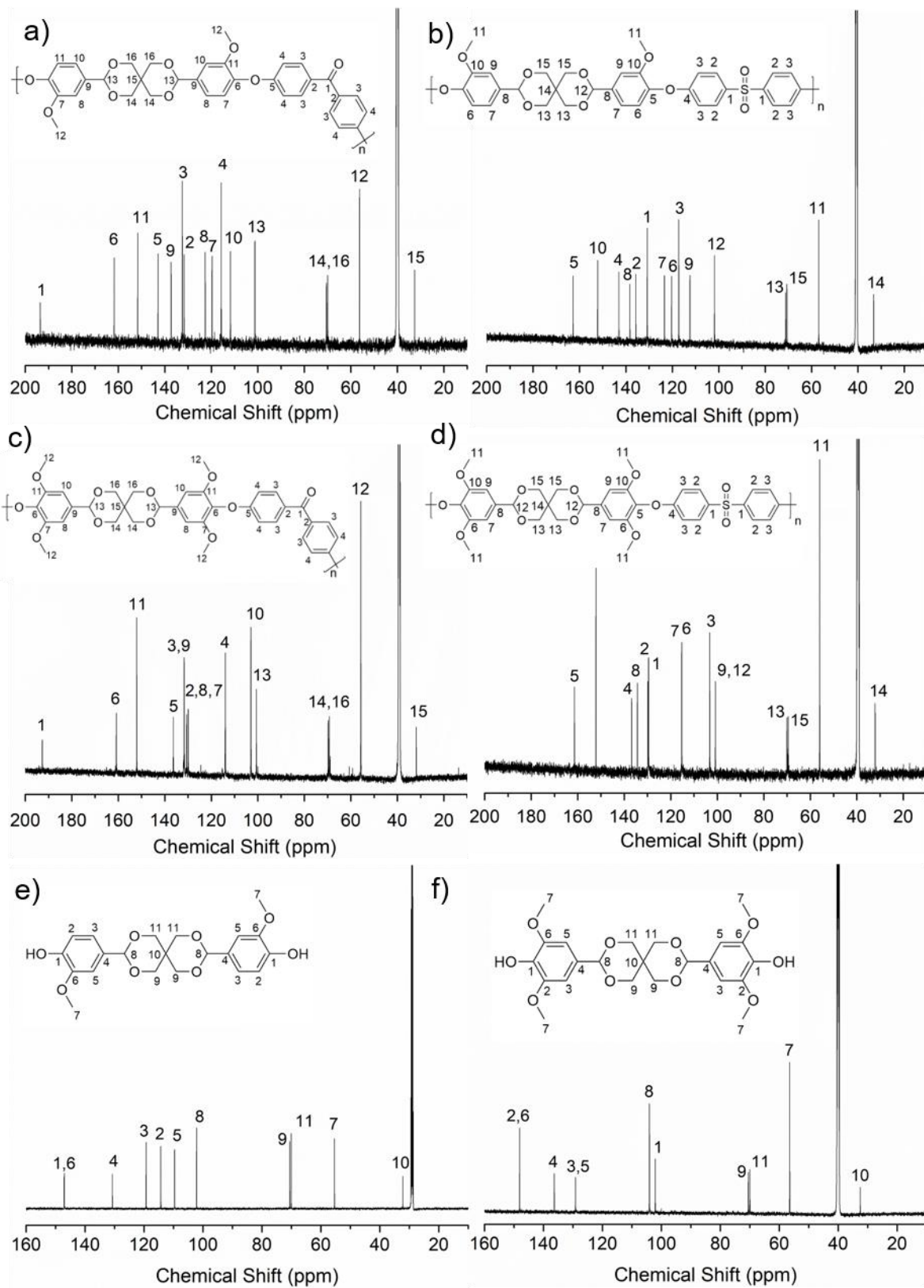**Figure S1**: ^{1}H NMR of (a) SPA, (b) VPA-DFS, (c) SPA-DFP, and (d) SPA-DFS (in *d*-DMSO).

Figure S2: ^{13}C NMR of (a) VPA-DFP, (b) VPA-DFS, (c) SPA-DFP, (d) SPA-DFS, (e) VPA, and (f) SPA (in *d*-DMSO).
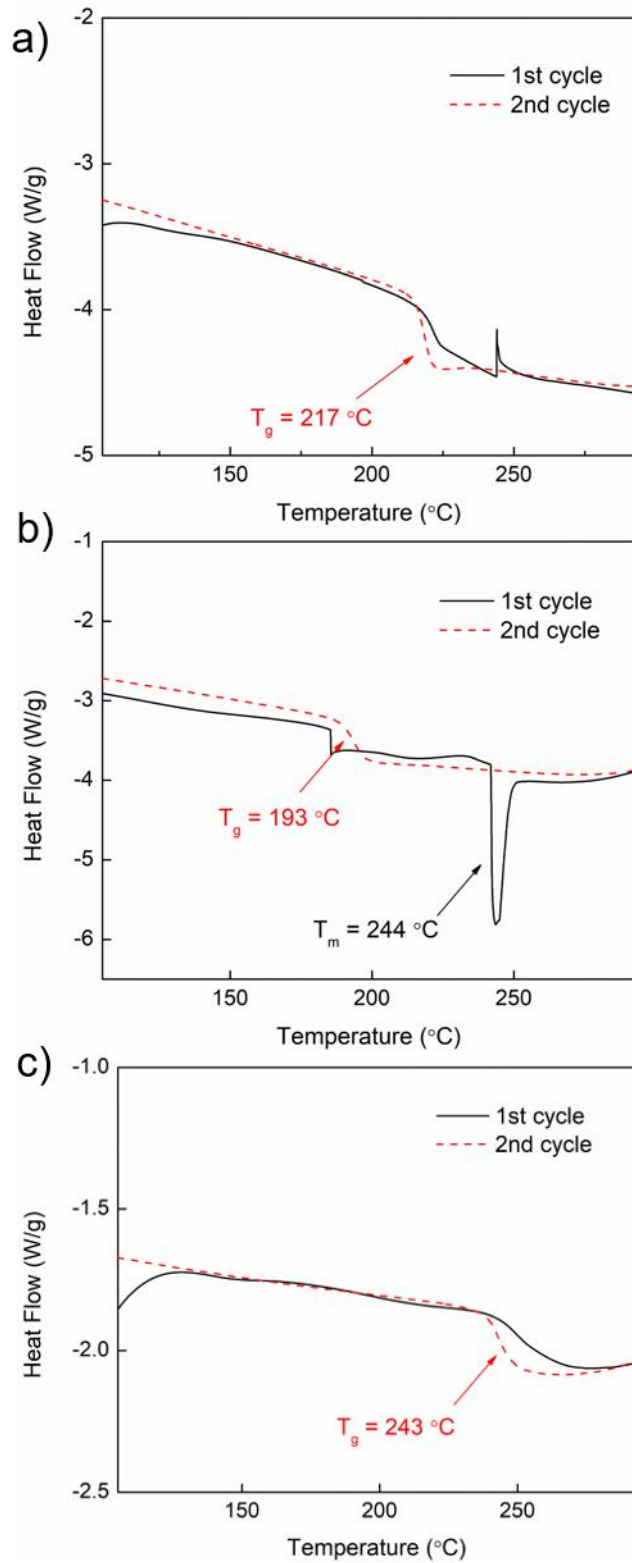
Figure S3: Heat flow vs. temperature obtained for (a) VPA-DFS, (b) SPA-DFP and (c) SPA-DFS using DSC.
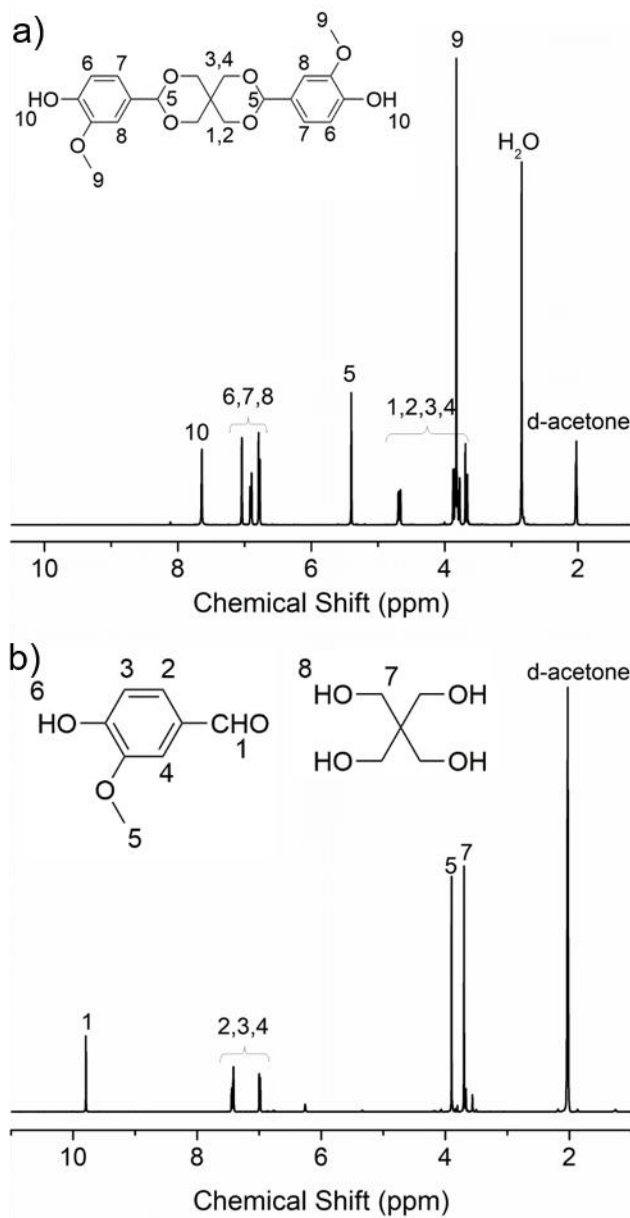
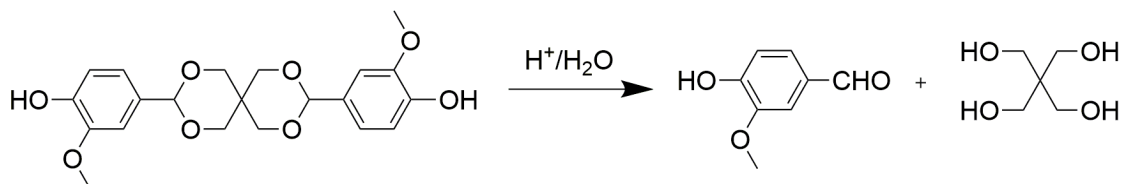**Figure S4**: ^{1}H NMR data obtained (a) before and (b) after the acid-catalyzed hydrolysis of VPA monomer in *d*-acetone/HCl (pH ~1) at room temperature after 1 h. Degradation experiments were conducted in 0.6 mL *d*-acetone containing 5 μL of 35 wt% aqueous HCl solution.

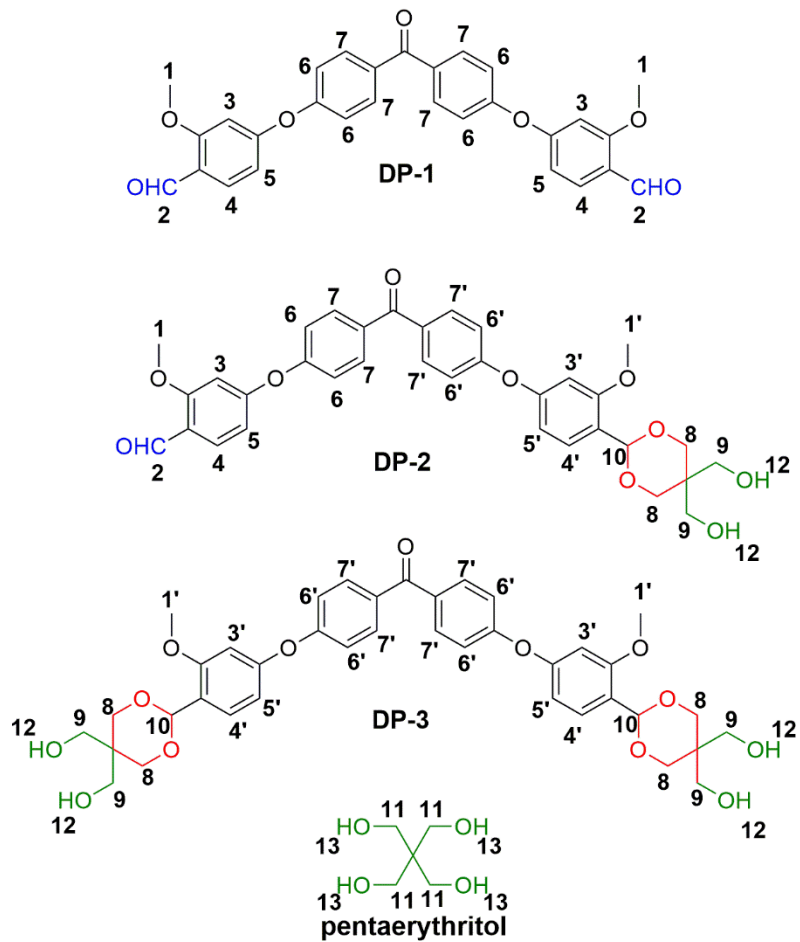**Scheme S1**: Mechanism of degradation of VPA monomer in acidic acetone.

Figure S5: Degradation products of VPA-DFP with labeled protons.
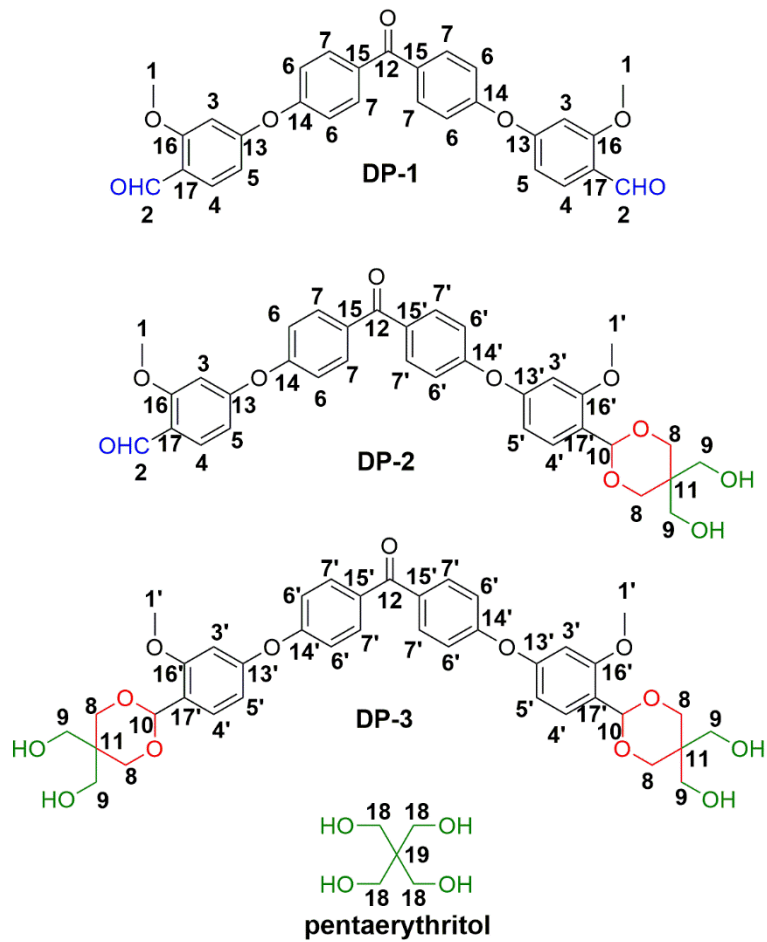
Figure S6: Degradation products of VPA-DFP with labeled carbons.
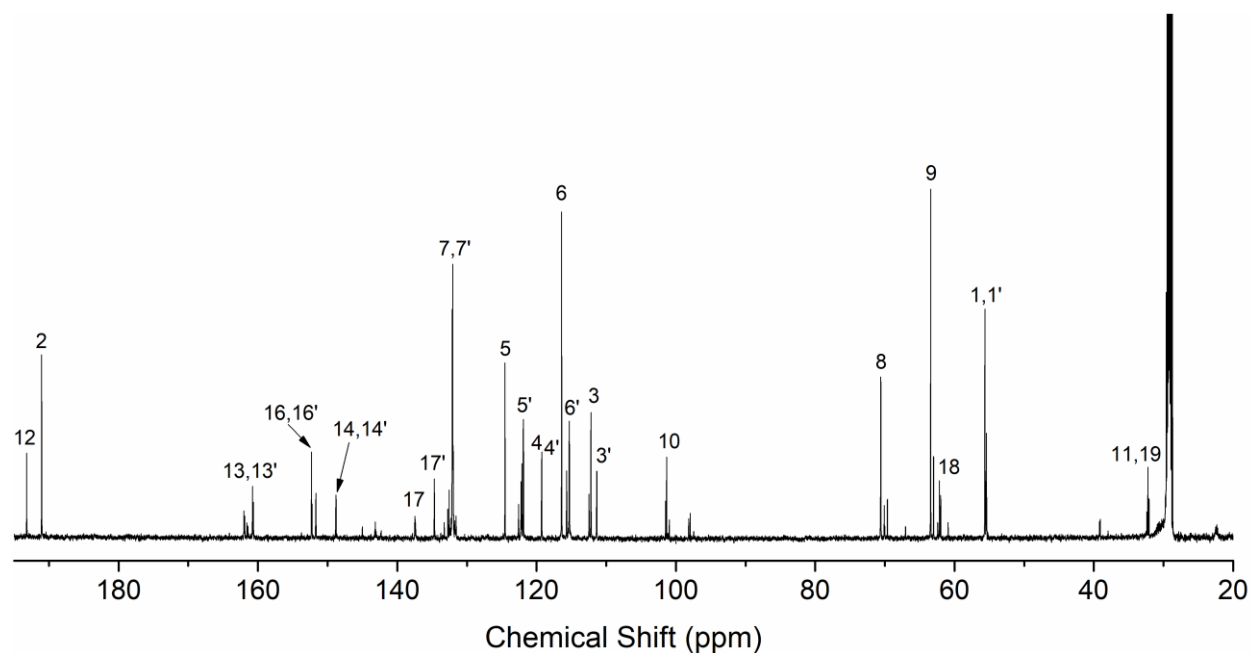
Figure S7: ^{13}C NMR of VPA-DFP after 24 h degradation in acidic acetone. Carbon labeling is reference in Figure S6. Degradation experiments were conducted in 0.6 mL *d*-acetone containing 5 µL of 35 wt% aqueous HCl solution.
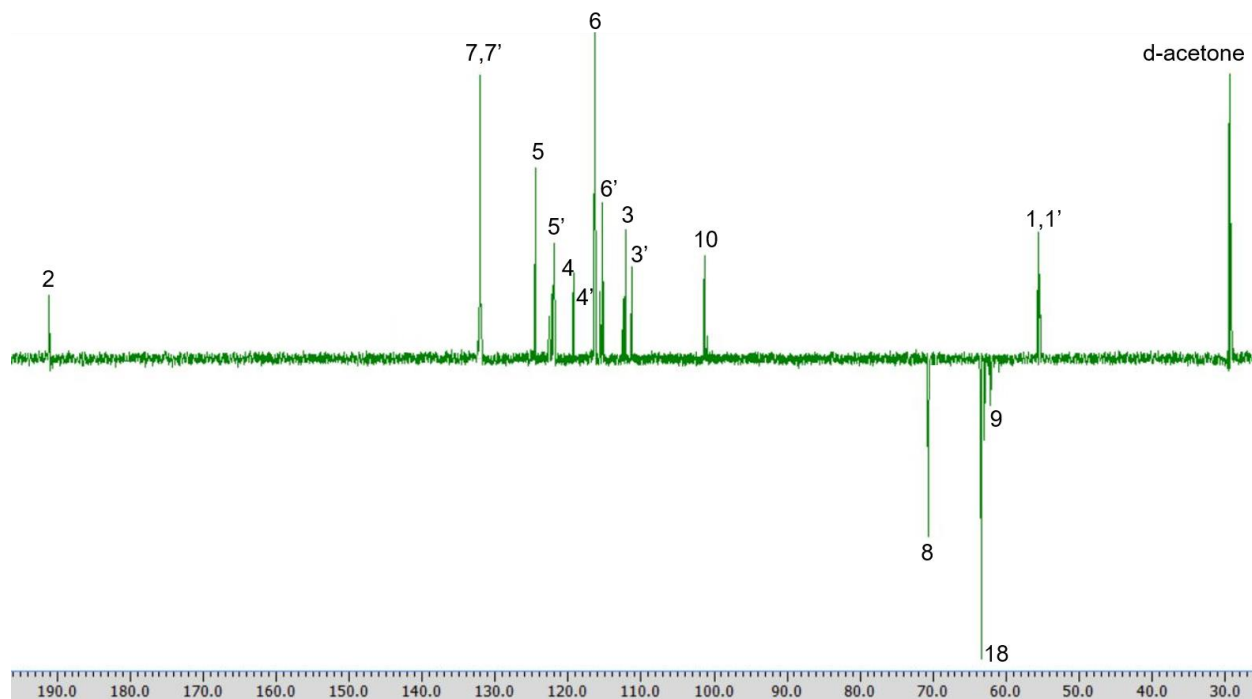
Figure S8: DEPT 135 of VPA-DFP after 24 h degradation in acidic acetone. Carbon labeling is referenced in Figure S6. Degradation experiments were conducted in 0.6 mL *d*-acetone containing 5 µL of 35 wt% aqueous HCl solution.

Figure S9: HMQC of VPA-DFP after 24 h degradation in acidic acetone. Degradation experiments were conducted in 0.6 mL *d*-acetone containing 5 µL of 35 wt% aqueous HCl solution.

Figure S10: COSY of VPA-DFP after 24 h degradation in acidic acetone. Degradation experiments were conducted in 0.6 mL *d*-acetone containing 5 µL of 35 wt% aqueous HCl solution.

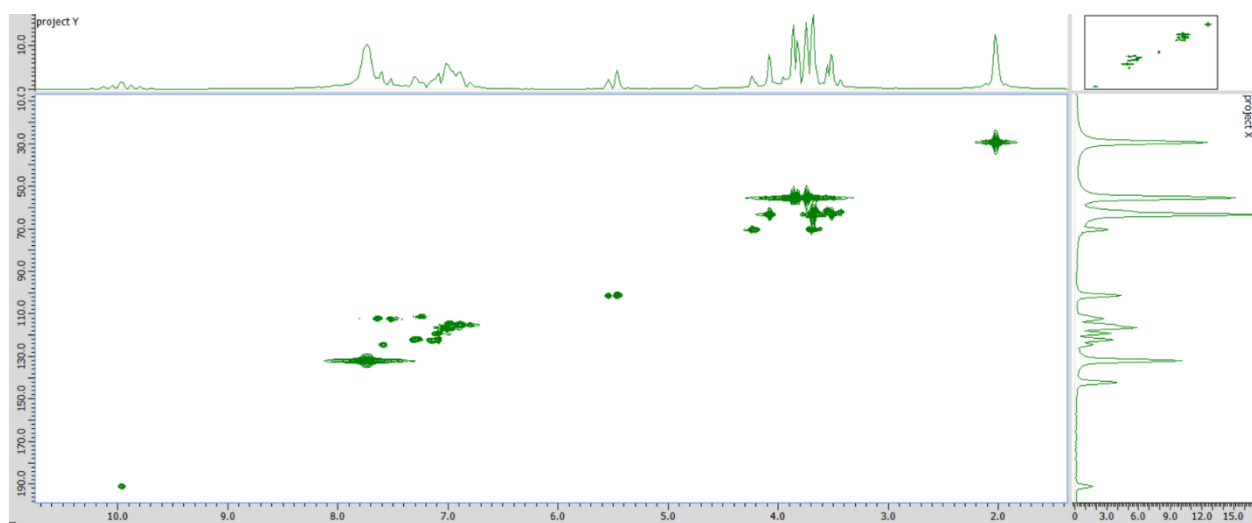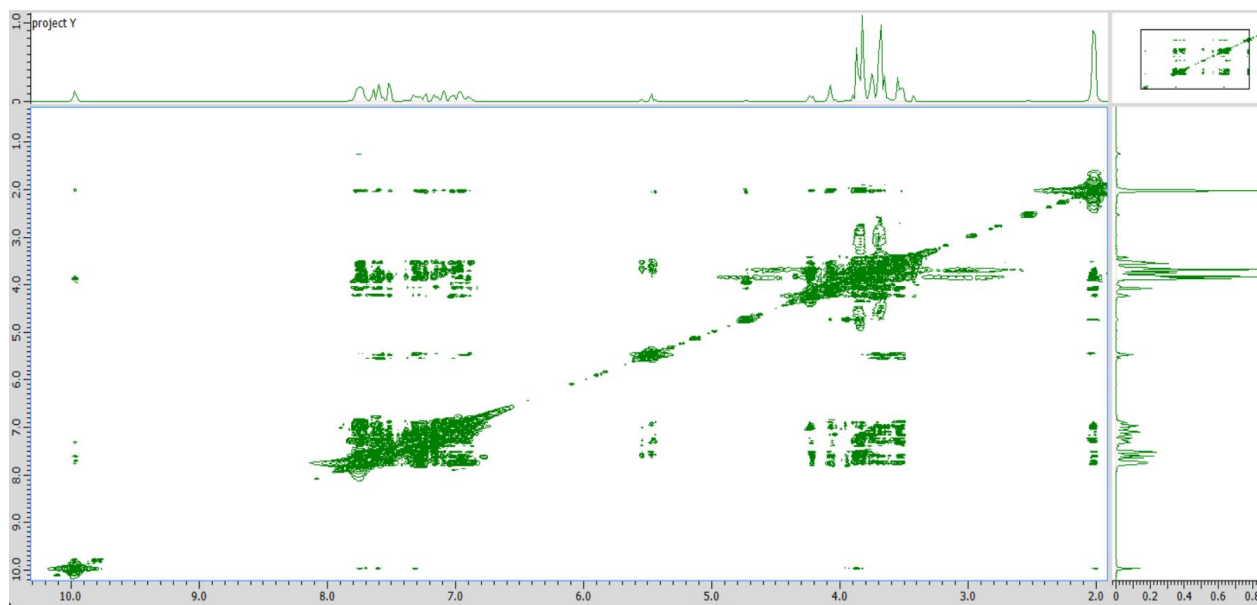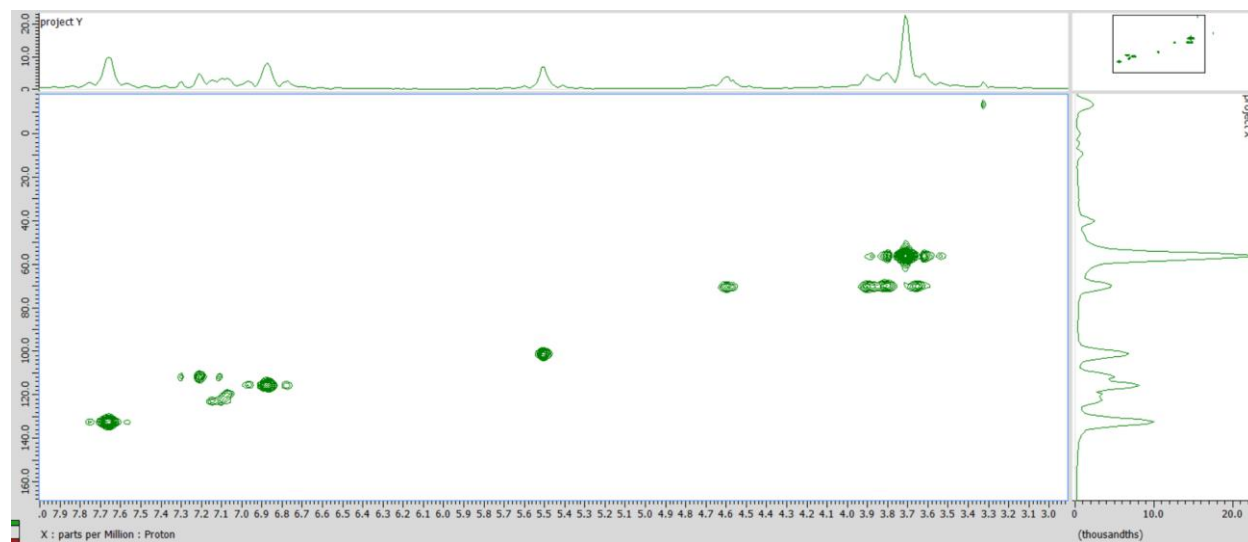**Figure S11**: HMQC of VPA-DFP prior to degradation.

<u>NMR Peak Assignments Determined through 2D NMR Analyses</u>

We used 2D NMR, including Distortions Enhancement by Polarization Transfer (DEPT 135), Correlated Spectroscopy (COSY), and Heteronuclear Multiple Quantum Coherence (HMQC) (**Figures S5-S11**), to assign peaks on the ^{1}H and ^{13}C spectra obtained from VPA-DFP after 24 h of degradation time in acidic acetone, shown in **Figures 1, 5, 7, S1 and S2**. The discussion below focuses on the presence of the four degradation products identified in **Scheme 3**: DP-1. DP-2, DP-3, and pentaerythritol. We note that oligomers may be present with the same functional end-groups as DP-1, DP-2, and DP-3. We therefore do not attempt to quantify the concentration of each degradation product, but rather concentrations of each of the relevant functional groups (described in the main text). DEPT experiments are used to distinguish between -CH$_3$, -CH$_2$ and -CH groups: -CH$_3$ and -CH peaks appear as normal, and -CH$_2$ peaks appear inverted. COSY experiments provide correlations when there is spin-spin coupling between neighboring protons. HMQC experiments provide information on coupling between connected protons and carbons.

By combining DEPT (**Figure S8**), HMQC (**Figure S9**) and COSY (**Figure S10**), we can assign the ^{1}H peaks obtained from VPA-DFP after 24 h degradation in acidic acetone (**Figure 5**, with peak labels in **Figure 5 and S5**), as well as the ^{13}C data (**Figure S7**, with labels in **Figure S6**). We start with the proton peak at 10.01 ppm. From the HMQC data, we see a correlation with the carbon peak at 191.1 ppm. We therefore assigned the peak to the aldehyde group (labeled peak 2).

The peaks at 5.48 and 5.58 ppm belong to the -CH in the acetal structure (peak 10). From HMQC data, we see a correlation with the carbon peak at 102 ppm, and from the DEPT data, we can observe the peak at 102 ppm is either -CH or -CH$_3$. Since the only expected -CH$_3$ group is a methoxy group, and would not be anticipated to be located at this ppm value, these results are consistent with the assignment of the proton peak at 5.48 and 5.58 ppm, and the carbon peak at 102 ppm, as the -CH in the acetal structure (peak 10). We note that in the COSY data there are correlations between the peaks at 5.48 and 5.58 ppm with peaks in the aromatic region (6.9-7.8 ppm) as well as the -CH$_2$ region at 3.5-4.2 ppm (-CH$_2$ and -OCH$_3$ peaks). We hypothesize that two -CH peaks (peak 10) are observed due to H-D exchange of the -CH with the deuterated acetone. Both peaks show the same correlations with other protons and carbons in the 2D data.

The peak at 4.7 ppm is assigned to the -OH group (peak 12). Correlations are observed in the COSY data with the -CH$_2$ peak at around 4-4.2 ppm (peak 9). Additionally, no correlations are observed for the proton at 4.7 ppm to carbons peaks in HMQC, consistent with the assignment of -OH.

We are assigning peaks in the range of 3.5 – 4.2 ppm to -CH$_2$ and -OCH$_3$ groups. From the HMQC data, we can see that these peaks are correlated with carbon peaks in the range of 55 – 65 ppm. We can see that there is one positive peak in the DEPT data at 56 ppm, indicating this is the

-OCH$_3$ peak (labeled peaks 1, 1'). The others are negative in the DEPT data, indicating -CH$_2$ peaks. Additionally, we observed correlations in the COSY data between the proton peak at 3.90 ppm and the aldehyde proton peak 2 at 10.01 ppm. Such correlations with the aldehyde peak were not observed for the proton peak at 3.72 ppm. We therefore assign peak 1 at 3.90 ppm and peak 1'at 3.72 ppm. With the help of COSY, peak 10 at 5.5 ppm is correlated with protons in the range of 3.6 - 3.75 ppm, indicating these protons are in close proximity. However, we do not see such correlations between peak 10 at 5.5 ppm and -CH$_2$ peaks at higher ppm values. As proton 10 is closer in proximity to proton 8 than it is to proton 9, we therefore assign proton 8 to the peaks at 3.6 - 3.75 ppm and proton 9 to the peaks at 4.1 – 4.2 ppm. Peak 11 also does not show correlations with peak 10, and we assign it to proton 11 on pentaerythritol. From the HMQC data, we can see that peak 1 on the ^{1}H spectrum (-OCH$_3$) is correlated with the peak at 56 ppm on the ^{13}C spectrum. Peak 1' on the ^{1}H spectrum is also correlated with the peak at 56 ppm on the ^{13}C spectrum. Peak 8 on the ^{1}H spectrum is correlated with the peak at 70 ppm on the ^{13}C spectrum, peak 9 on the ^{1}H spectrum is correlated with the peak at 63 ppm on the ^{13}C spectrum, and peak 11 on the ^{1}H spectrum is correlated with the peak at 62 ppm on the ^{13}C spectrum. We thus assigned the peaks in the carbon spectrum in this manner.

Next, we will discuss aromatic peaks in the range of 6.9 – 7.8 ppm in **Figure 5**. Protons 6 and 7 were assigned in the ^{1}H NMR spectrum based on reported data for the DFP monomer.[1] Upon examining HMQC data of both the degradation product mixture (**Figure S9**) and VPA-DFP prior to degradation (**Figure S11**), we observed correlations between the aromatic proton and carbon peaks: proton 6 at 7.8 ppm is correlated with carbon 6 at 118.2 ppm and carbon 6' at 117.7 ppm, and proton 7 at 6.9 ppm is correlated with carbon 7 at 130.9 ppm and carbon 7' at 130.8 ppm. We now continue to the aromatic protons labeled 3, 4, 5 on DP-1 and DP-2 which are near the aldehyde

proton. In the COSY data, we found several spots at 7.3 ppm, 7.6 ppm and 7.7 ppm (which are attributed to protons 3, 4, and 5, though they cannot be distinguished from one another) which are correlated to the aldehyde proton at 10.01 ppm, indicating close proximity. We therefore label these as the aromatic protons located next to the aldehyde group. However, protons 3', 4' and 5' (at 7.0, 7.2, and 7.6 ppm) were not correlated with the aldehyde proton, and instead were correlated with peak 10 (at 5.5 ppm) on the partially hydrolyzed acetal group. Therefore, protons 3', 4' and 5' are the aromatic protons in closest proximity to the partially hydrolyzed acetal group. We observed correlations between the aromatic proton and carbon peaks in HMQC data: protons 3, 4, 5 at 7.3, 7.6, 7.7 ppm are correlated with carbons 3, 4, 5 at 111.3, 119.7 and 124.5 ppm, respectively and carbons 3', 4', 5' at 100.8, 119.6, and 121.9 ppm, respectively. The peaks for carbons 3, 4 and 5 were assigned based on examining reported data of ^{13}C NMR of vanillin,[2] ^{13}C NMR of VPA (**Figure S2e**), ^{13}C NMR of VPA-DFP (**Figure S2a**) and HMQC data of VPA-DFP prior to degradation (**Figure S11**). We also noticed a shift of 3, 4 and 5 to the left of peaks 3', 4' and 5'. We assigned the peak of carbons for 3', 4' and 5' upon considering reported data of ^{13}C NMR of vanillin and ^{13}C NMR data of VPA (**Figure S2e**). As a result, the cleavage of acetal group and formation of aldehyde group would shift the carbons on the neighboring aromatic rings to the left. We note that all of the assigned aromatic carbon peaks are positive in the DEPT data.

Table S1: Molecular weight at the peak maxima[a] (M_p, kg/mol) quantified for each peak observed in GPC data obtained from the acid-catalyzed hydrolysis of VPA-DFP in *d*-acetone/HCl (pH ~1) at room temperature. For comparison purposes, the known molecular weight of each small molecule is summarized in **Table S2**.

	First Peak (26.8 min): attributed to oligomeric species	Second Peak (27.2 min): attributed to DP-3	Third Peak (27.7 min): attributed to DP-2	Fourth Peak (28.8 min): attributed to DP-1	Fifth Peak (30.1 min): attributed to pentaerythritol
0.5 h	2.9	0.8	0.6	0.5	0.1
1 h	2.7	0.8	0.6	0.5	0.1
3 h	2.7	0.8	0.6	0.4	0.1
6 h	2.7	0.8	0.6	0.4	0.1
10 h	2.7	0.8	0.6	0.4	0.1
24 h	2.7	0.8	0.6	0.4	0.1

[a] Quantified using a calibration curve derived from polystyrene standards

Table S2: Molecular weights of degradation products

Degradation Product	Molecular weight (g/mol)
DP-1	482.1
DP-2	600.2
DP-3	718.3
Pentaerythritol	136.1

Hansen Solubility Parameters of Degradation Products and Solvents

All functional groups are divided into first order groups that comprise the basic molecular structures of the compounds and second order groups defined by conjugation theory. The dispersion solubility parameter (δ_d), polar solubility parameter (δ_p) and hydrogen bonding solubility parameter (δ_{hb}) are calculated by the following equations:[3]

$$\delta_d = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 17.3231\right) MPa^{0.5} \qquad \text{(eqn. S1)}$$

$$\delta_p = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.3548\right) MPa^{0.5} \qquad \text{(eqn. S2)}$$

$$\delta_{hb} = \left(\sum_i N_i C_i + W \sum_j M_j D_j + 7.9793\right) MPa^{0.5} \qquad \text{(eqn. S3)}$$

where C_i is the contribution of the first-order group of type i that appears N_i times in the compound and D_j is the contribution of the second-order group of type j that appears M_j times in the compound, and δ is calculated as:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_{hb}^2} \qquad \text{(eqn. S4)}$$

Degradation Products of VPA-DFP:

Chemical structures of the degradation products are shown in Figure 5 of the main text.

AC refers to an aromatic carbon in the descriptions below.

DP-1:

First-order groups: 2 –CHO, 2 –OCH₃, 1 CO, 2 O, 10 AC, 14 ACH

Second-order group: 2 ACHO, 2 ACOAC

$$\delta_d = -0.403 * 2 - 2 * 0.5828 - 0.4343 + 2 * 0.0472 + 10 * 0.8446 + 14 * 0.1105 + 17.3231 = 24.6298 \ MPa^{0.5} \qquad \text{(eqn. S5)}$$

$$\delta_p = 3.4734 * 2 + 2 * 0.1764 + 0.7905 + 2 * 3.3432 + 10 * 0.6187 - 14 * 0.5303 + +7.3548 = 10.4063 \ MPa^{0.5} \qquad \text{(eqn. S6)}$$

$$\delta_{hb} = 0.1687 * 2 + 2 * 0.146 + 1.8147 + 2 * 0.0256 + 10 * 0.0084 - 14 * 0.4305 + 7.9793 = 6.3410 \ MPa^{0.5} \qquad \text{(eqn. S7)}$$

$$\delta = 27.5 \ MPa^{0.5}$$

DP-2:

First order groups: 1 –CHO, 2 –OCH₃, 1 CO, 2 O, 10 AC, 14 ACH, 2 –OH, 1 –C, 2 –CH₂, 1 –CH, 2 –OCH₂

Second order groups: 1 ACHO, 2 ACOAC

$\delta_d = -0.403 - 2*0.5828 - 0.4343 + 2*0.0472 + 10*0.8446 + 14*0.1105 - 2*0.3462 + 1.2686 - 2*0.0269 + 0.645 + 2*0.031 + 0.3772 - 2*0.5646 + 17.3231 = 18.9383\ MPa^{0.5}$

(eqn. S8)

$\delta_p = 3.4734 + 2*0.1764 + 0.7905 + 2*3.3432 + 10*0.6187 - 14*0.5303 + 2*1.1404 + 2.0838 - 2*0.3045 + 0.6491 + 2*0.8826 - 1.811 - 2*3.4329 + 7.3548 = 14.9138\ MPa^{0.5}$

(eqn. S9)

$\delta_{hb} = 0.1687 + 2*0.146 + 1.8147 + 2*0.0256 + 10*0.0084 - 14*0.4305 + 2*7.1908 + 0.0866 - 2*0.4119 - 0.2018 - 2*0.1528 - 1.0096 + 2*2.083 + 7.9793 = 20.7\ MPa^{0.5}$

(eqn. S10)

$\delta = 36.3\ MPa^{0.5}$

DP-3:

First order groups: 2 –OCH$_3$, 1 CO, 2 O, 10 AC, 14 ACH, 4 –OH, 2 –C, 4 –CH$_2$, 2 –CH, 4 –OCH$_2$

Second order groups: 2 ACOAC

$\delta_d = -2*0.5828 - 0.4343 + 2*0.0472 + 10*0.8446 + 14*0.1105 - 4*0.3462 + 2*1.2686 - 4*0.0269 + 2*0.645 + 4*0.031 - 2*0.5646 + 17.3231 = 27.1402\ MPa^{0.5}$

(eqn. S11)

$\delta_p = 2*0.1764 + 0.7905 + 2*3.3432 + 10*0.6187 - 14*0.5303 + 4*1.1404 + 2*2.0838 - 4*0.3045 + 2*0.6491 + 4*0.8826 - 2*3.4329 + 7.3548 = 19.4213\ MPa^{0.5}$

(eqn. S12)

$\delta_{hb} = 2*0.146 + 1.8147 + 2*0.0256 + 10*0.0084 - 14*0.4305 + 4*7.1908 + 2*0.0866 - 4*0.4119 - 2*0.2018 - 4*0.1528 + 2*2.083 + 7.9793 = 34.6342\ MPa^{0.5}$

(eqn. S13)

$\delta = 48.1\ MPa^{0.5}$

Pentaerythritol:

First-order groups: 4 –OH, 1 –C, 4 –CH$_2$

$\delta_d = 4*-0.3462 + 1.2686 - 4*0.0269 + 17.3231 = 17.0993\ MPa^{0.5}$

(eqn. S14)

$\delta_p = 4*1.1404 + 2.0838 - 4*0.3045 + 7.3548 = 12.7822\ MPa^{0.5}$

(eqn. S15)

$\delta_{hb} = 4*7.1908 + 0.0866 - 4*0.4119 + 7.9793 = 35.1815\ MPa^{0.5}$

(eqn. S16)

$\delta = 41.2 \, MPa^{0.5}$

Pure Solvents:

Acetone:

First-order groups: 1 CH$_3$CO–, 1 –CH$_3$

Second-order group: 1 CH$_3$C=

$$\delta_d = -0.3551 - 0.9714 - 0.0785 + 17.3231 = 15.9175 \, MPa^{0.5} \qquad \text{(eqn. S17)}$$

$$\delta_p = -1.6448 + 2.3192 + 0.3316 + 7.3548 = 8.3608 \, MPa^{0.5} \qquad \text{(eqn. S18)}$$

$$\delta_{hb} = -0.7813 - 1.3078 + 0.3875 + 7.9793 = 5.5765 \, MPa^{0.5} \qquad \text{(eqn. S19)}$$

$\delta = 19.9 \, MPa^{0.5}$

DMSO:

First-order groups: 1 S, 2 –CH$_3$, 1 O

$$\delta_d = 1.4899 - 2*0.9714 + 0.0472 + 17.3231 = 16.9174 \, MPa^{0.5} \qquad \text{(eqn. S20)}$$

$$\delta_p = 9.2072 - 2*1.6448 + 3.3432 + 7.3548 = 16.6156 \, MPa^{0.5} \qquad \text{(eqn. S21)}$$

$$\delta_{hb} = -0.625 - 2*0.7813 + 0.0256 + 7.9793 = 5.8173 \, MPa^{0.5} \qquad \text{(eqn. S22)}$$

$\delta = 24.4 \, MPa^{0.5}$

_H$_2$O_:

$\delta = 47.8 \, MPa^{0.5}$

References:

1. S.-A. Park, H. Jeon, H. Kim, S.-H. Shin, S. Choy, D. S. Hwang, J. M. Koo, J. Jegal, S. Y. Hwang, J. Park and D. X. Oh, *Nature Communications*, 2019, **10**, 2601.
2. S. Ma, J. Wei, Z. Jia, T. Yu, W. Yuan, Q. Li, S. Wang, S. You, R. Liu and J. Zhu, *Journal of Materials Chemistry A*, 2019, **7**, 1233-1243.
3. E. Stefanis and C. Panayiotou, *International Journal of Thermophysics*, 2008, **29**, 568-585.