Supporting Information for

Synthesis and thermally induced structural transformation of phthalimide and nitrile-functionalized benzoxazine: toward smart ortho-benzoxazine chemistry for low flammability thermosets

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Synthesis of 2-(2-Hydroxyphenyl)-isoindoline-1,3-dione (o-PP)

Into a 250 mL round flask were placed phthalic anhydride (7.41 g, 0.05 mol), o-aminophenol (5.41 g, 0.05 mol), and 60 ml of acetic acid. The mixture was stirred and refluxed for 6 h. After cooling to room temperature, the precipitate was filtered and washed with 200 mL of methanol. Removal of solvent by evaporation afforded an orange crystal (yield ca. 90%). $^1$H NMR (DMSO), ppm: $\delta = 6.82-7.93$ (8H, Ar), 9.76 (OH). IR spectra (KBr, cm$^{-1}$) = 3383 (O-H stretching), 1787, 1700 (Imide I), 1390 (imide II, C-N stretching), 722 (C=O bending).

Synthesis of 2-(3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-8-yl)-isoindoline-1,3-dione (oPP-a)

Into a 100 mL round flask were added 30 mL of xylenes, aniline (1.40 g, 0.15mol), o-PP (3.59 g, 0.015mol), and paraformaldehyde (0.91g, 0.03 mol). The mixture was stirred at 120 °C for 6 h. The mixture was cooled to room temperature and precipitated into 100 mL of methanol. Removal of solvent by filtering afforded a yellow powder. (yield ca. 95%, m.p. 209 °C). $^1$H NMR (DMSO), ppm: $\delta = 4.72$ (s, Ar-CH$_2$-N, oxazine), 5.42 (s, O-CH$_2$-N, oxazine), 6.85-7.96 (12H, Ar). IR spectra (KBr), cm$^{-1}$: 1774, 1719 (Imide I), 1497 (stretching of trisubstituted benzene ring), 1385 (Imide II), 1231 (C-O-C asymmetric stretching), 1179 (C-N-C asymmetric stretching), 924 (out-of-plane C-H).
Figure S1. $^1$H NMR spectrum of oPP.

Figure S2. $^{13}$C NMR spectrum of oPP.
Figure S3. $^1$H NMR spectrum of oPP-a.

Figure S4. $^{13}$C NMR spectrum of oPP-a.
Figure S5. $^1$H-$^{13}$C HMOC spectrum of oPP-an.

Figure S6. DSC curves of oPP-a at different heating rates.
Figure S7. Representations of Kissinger and Ozawa methods for the calculation of activation energy for oPP-a.

Table S1. The Activation Energy of oPP-a obtained by Kissinger and Ozawa Methods.

| Sample | Kissinger $E_a$ (kJ/mol) | Ozawa $E_a$ (kJ/mol) |
|--------|--------------------------|---------------------|
| oPP-a  | 86.0                     | 89.5                |