Supporting Information

Smart and Sustainable Design of Latent Catalyst-Containing Benzoxazine-Bio-Resins and Application Studies

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Scheme S1. Synthesis of BA-a and RES-fa.

Figure S1. FT-IR spectrum of NAR-fa.
Figure S2. 2D $^1$H-$^1$H NOESY NMR spectrum of NAR-fa.

Figure S3. 2D $^1$H-$^{13}$C HMQC NMR spectrum of NAR-fa.
Figure S4. *In situ* FT-IR spectra of NAR-fa during the step by step polymerization reaction.

Figure S5. $^1$H NMR spectrum of NAR-fa in DMSO-$d_6$. 
Figure S6. DSC thermograms of NAR-fa (in black, bottom), the one pretreated at 60 °C for 1h (in red, middle), and that pretreated at 100 °C for 1h (in blue, top).

Figure S7. 1H NMR spectra of NAR-fa in CDCl₃ and that stored in the dark for 3 months.
**Figure S8.** $^1$H NMR spectra of NAR-fa in DMSO-$d_6$ and that stored in the dark for 3 months.

**Figure S9.** Thermomechanical analysis of poly(NAR-fa).
Figure S10. TGA (—) and DTG (⋯⋯) thermograms of poly(NAR-fa) under nitrogen (a) and air (b) atmospheres.

Figure S11. Microscale combustion calorimetric (MCC) analysis of poly(NAR-fa). Plots of the total heat release as a function of the temperature.
Table S1. Thermal and fire related properties of poly(NAR-fa).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (TMA) ($^\circ$C)</th>
<th>$T_g$ (DMA) ($^\circ$C)</th>
<th>$T_{as}$ (°C)</th>
<th>$T_{ato}$ (°C)</th>
<th>$Yc$ (%)</th>
<th>$T_{as}$ (°C)</th>
<th>$T_{ato}$ (°C)</th>
<th>$Yc$ (%)</th>
<th>HRC (Jg$^{-1}$K$^{-1}$)</th>
<th>THR (KJg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(NAR-fa)</td>
<td>278</td>
<td>286</td>
<td>361</td>
<td>404</td>
<td>64</td>
<td>360</td>
<td>407</td>
<td>2</td>
<td>31.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Figure S12. DSC thermograms of benzoxazine resins (BA-a and BA-a/NAR-fa blend).

Figure S13. DSC thermograms of benzoxazine resins (RES-fa and RES-fa/NAR-fa blend).
blend).

**Figure S14.** Dynamic mechanical analysis of polybenzoxazines.

**Figure S15.** TGA (—) thermograms of polybenzoxazines under nitrogen atmosphere.
Figure S16. Microscale combustion calorimetric (MCC) analysis of polybenzoxazines. Plots of the heat release rate (a) and total heat release (b) as a function of the temperature.