## Supporting Information (SI)

# Engineering lignin-derivable diacrylate networks with tunable architecture and mechanics 

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## Abbreviations

BGF
BGFDA
BA
DCM
$E_{\mathrm{t}}$
$T_{\mathrm{d}, 5 \%}$
$T_{\mathrm{g}}$
VDA
$\varepsilon_{B}$
$\sigma_{M}$

Bisguaiacol F
Bisguaiacol F diacrylate
n-butyl acrylate
Dichloromethane
Young's modulus
Degradation temperature at $5 \mathrm{wt} \%$ loss
Glass transition temperature
Vanillyl alcohol diacrylate
Elongation-at-break
Ultimate tensile strength

Proton ( ${ }^{1} \mathrm{H}$ ) Nuclear Magnetic Resonance (NMR) spectra for lignin-derivable building blocks in deuterated chloroform $\left(\mathrm{CDCl}_{3}\right)$


Fig. S1 ${ }^{1} \mathrm{H}$ NMR spectrum of bisguaiacol F


Fig. S2 ${ }^{1} \mathrm{H}$ NMR spectrum of vanillyl alcohol diacrylate




Fig. S3 ${ }^{1} \mathrm{H}$ NMR spectrum of bisguaiacol F diacrylate


$$
\dot{F}+\frac{98}{\dot{q}}
$$

$$
\underbrace{a}_{b}
$$



Fig. S4 ${ }^{1} \mathrm{H}$ NMR spectrum of $n$-butyl acrylate

## Film curing steps and film appearances



Fig. S5 Schematic representation of film casting and curing procedures


30 mm

Fig. S6 Optical images of each acrylate networks after thermal post-curing with a film thickness $\sim 0.2 \mathrm{~mm}$

## Differential scanning calorimetry (DSC) results for curing of acrylate networks



Fig. S7 DSC curve of acrylate networks (a) before and (b) after thermal post-curing (exotherm up, $10{ }^{\circ} \mathrm{C} / \mathrm{min}, \mathrm{N}_{2}$ ). Exothermic peaks in (a) were applied to determine the temperature for thermal post-curing.

## Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra for acrylate networks



Fig. S8 Stacked ATR-FTIR spectra of acrylate networks before and after thermal post-curing. The conversion was probed quantitatively by the disappearance of the acrylate carbon double bond stretching band at $\sim 1635 \mathrm{~cm}^{-1}$ (highlighted in red) with an internal reference of carbonyl double bond stretching band at $\sim 1724 \mathrm{~cm}^{-1}$ (128 scans, resolution $4 \mathrm{~cm}^{-1}$ ).

Thermogravimetric analysis (TGA) results of acrylate networks


Fig. S9 Thermogravimetric analysis traces and respective first-derivative curves of acrylate networks for (a) varying diacrylate content and (b) varying diacrylates ( $10{ }^{\circ} \mathrm{C} / \mathrm{min}, \mathrm{N}_{2}$ ).

Table S1 $T_{\mathrm{d}, 5 \%}$ of acrylate networks.

| Sample | $T_{\mathrm{d}, 5 \%}\left({ }^{\circ} \mathrm{C}\right)$ |
| :---: | :---: |
| VDA/BA-25/75 | 363 |
| VDA/BA-50/50 | 367 |
| VDA/BA-75/25 | 361 |
| BGFDA/BA-25/75 | 376 |
| BGFDA/BA-50/50 | 378 |
| VDA/BGFDA/BA-25/25/50 | 222 |



Fig. S10 Conversion profile of VDA/BA networks at different curing times as an example of the evolution of network formation. Each data point represents the triplicated result using samples from different batch.
(a)

(b)


Fig. S11 Structures used to predict $T_{\mathrm{g}} \mathrm{S}$ of the homopolymer for (a) VDA and (b) BGFDA via Polymer Genome. ' $g$ ' represents the bond with repeated units, and side groups marked with red dashed circle denote the structure added manually to mimic crosslinked structure. The predicted $T_{\mathrm{g}}$ for VDA homopolymer is $194^{\circ} \mathrm{C}$ and BGFDA homopolymer is $222^{\circ} \mathrm{C}$.


Fig. S12 Small-angle X-ray scattering spectra for VDA/BA networks. Curves are based on absolute scale and shifted vertically for clarity (sample-to-detector distance: 1200 mm ).


Fig. S13 Uniaxial tensile curves of acrylate networks for (a) full scale and (b) scale in the low strain region.

Table S2 Uniaxial tensile properties of acrylate networks

|  | $E_{\mathrm{t}}(\mathrm{GPa})$ | $\varepsilon_{B}(\%)$ | $\sigma_{M}(\mathrm{MPa})$ | Toughness ( $\mathrm{MJ} \mathrm{m}^{-3}$ ) |
| :---: | :---: | :---: | :---: | :---: |
| VDA/BA-25/75 | $1.3 \pm 0.1$ | $4.3 \pm 1.6$ | $40.6 \pm 6.3$ | $1.1 \pm 0.5$ |
| VDA/BA-50/50 | $2.0 \pm 0.4$ | $1.6 \pm 0.3$ | $28.8 \pm 4.0$ | $0.3 \pm 0.1$ |
| VDA/BA-75/25 | $2.0 \pm 0.8$ | $1.9 \pm 0.4$ | $32.6 \pm 5.8$ | $0.3 \pm 0.1$ |
| BGFDA/BA-25/75 | $0.8 \pm 0.2$ | $4.4 \pm 0.2$ | $28.6 \pm 1.2$ | $0.7 \pm 0.1$ |
| BGFDA/BA-50/50 | $1.5 \pm 0.1$ | $1.8 \pm 0.3$ | $25.4 \pm 1.5$ | $0.3 \pm 0.1$ |
| $\begin{gathered} \text { VDA/BGFDA/BA- } \\ 25 / 25 / 50 \end{gathered}$ | $1.4 \pm 0.1$ | $2.3 \pm 0.3$ | $30.7 \pm 3.3$ | $0.4 \pm 0.1$ |

