## Supporting Information

Polybutadiene vitrimers based on dioxaborolane chemistry and dual networks with static and dynamic crosslinks

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1) Grafting characterization

1. NMR characterization of **BE-SH** and **Bis-BE-SH**

**Figure S1.** $^1$H NMR spectrum of **BE-SH** in CDCl$_3$.

**Figure S2.** $^{13}$C NMR spectrum of **BE-SH** in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of Bis-BE-SH in CDCl$_3$.

Figure S4. $^{13}$C NMR spectrum of Bis-BE-SH in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of neat PB in CDCl$_3$.

2. Equations related to radical grafting

Equation S1 $f(\%) = \frac{\text{Integration proton } d}{(\text{Integration all protons} - 11 \times \text{Integration proton } d)/6}$

Equations S2 $\text{grafting yield (\%) = } \frac{\text{Integration proton } d \text{ after precipitation}}{\text{Integration proton } d \text{ before precipitation}}$

Equation S3 $\text{vinyl (\%) = } \frac{(\text{Integration proton } q)/2}{(\text{Integration all protons} - 11 \times \text{Integration proton } d)/6}$

Equation S4 $\text{vinylene (\%) = } \frac{((\text{Integration proton } m+p)-\text{Integration proton } q)/2}{(\text{Integration all protons} - 11 \times \text{Integration proton } d)/6}$
3. Intramolecular cyclizations

Scheme S1. Schemes for the different pathways to intramolecular cyclizations.

4. SEC characterization of grafted PB

Figure S6. SEC chromatograms of neat PB (black), PB-BE-5 (blue) and PB-BE-9 (red).
2) Vitrimers and static networks characterization

1. FTIR characterization of **PB-BE-V5**

![FTIR spectra of PB-BE-V5 (blue), neat polybutadiene PB (red) and Bis-BE-SH (black).](image)

**Figure S7.** FTIR spectra of PB-BE-V5 (blue), neat polybutadiene PB (red) and Bis-BE-SH (black).

2. Swelling ratios and insoluble fractions for vitrimers and static networks

![Swelling ratios and insoluble fractions](image)

**Figure S8.** Swelling ratios and insoluble fraction in toluene after 24h at room temperature.
3. SEC characterization of PB, PB-g-BE and Vitrimers cleaved by diolysis

![SEC chromatograms](image)

**Figure S9.** SEC chromatograms of **PB-BE-V5** after diolysis (red), **PB-BE-5** (blue, dashed) and PB (black).

4. DMA characterization, DSC characterization, TGA characterization and stress relaxation experiments

![Tan delta graph](image)

**Figure S10.** Tan delta of static networks (dashed lines) and vitrimers (solid lines) as a function of temperature and for various crosslinking densities.
Figure S11. DSC curves of static networks (dashed lines) and vitrimer (solid lines) with various crosslinking densities, and of the polybutadiene precursor.

Figure S12. Thermogravimetric analysis of the polybutadiene precursor (black) and of vitrimer (solid line) and their static network counterparts (dashed line) with various crosslinking densities. Left: From 25 °C to 500 °C. Right: From 350 to 500 °C.
Figure S13. Stress relaxation of PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) vitrimers at different temperatures.
Figure S14. Plots of $\ln(\tau)$ and $\ln(\eta)$ versus $1000/T$ for PB-BE-V5 vitrimer.

Plot of $\ln(\eta)$ and $\ln(\tau)$ versus $1000/T$ for PB-BE-V5 and linear fits to extract the activation energy on viscosity $E_a = 32.5$ kJ/mol and on relaxation time $E_a = 38.9$ kJ/mol. Viscosities were extracted from stress relaxation data with Equation 3. Relaxation times were extracted from stress relaxation data with Equation 4.
3) Vitrimer recycling

1. Mechanical properties of vitrimers

![Graphs showing mechanical properties of vitrimers](image)

**Figure S15.** Tensile stress-strain curves at 25 °C for initial and recycled (up to 3 times) PB-BE-V5. Results on multiple specimens (N = 5 specimens tested in all cycles of recycling) are shown for reproducibility.
Figure S16. Young modulus before and after recycling up to three times of PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) vitrimers.

2. DSC and TGA characterizations before and after recycling

Figure S17. DSC analysis before (solid lines) and after three recycling (dashed lines) of PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) vitrimers.
Figure S18. Thermogravimetric analysis of vitrimers PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) as synthesized and after 3 recycling cycles, and of the polybutadiene precursor (black). Left: From 25 °C to 500 °C. Right: From 350 to 500 °C.

3. SEC characterization before and after recycling

Figure S19. SEC chromatograms before (solid lines) and after three recycling (dashed lines) of PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) vitrimers. After diolysis for all specimens.
4) Creep experiments on vitrimers

**Figure S20.** Consecutive elongational creep-recovery experiments for PB-BE-V3 vitrimer: 30 min of creep under a stress of 0.01 MPa followed by 30 min of recovery at 60 °C.

**Figure S21.** Consecutive elongational creep-recovery experiments for PB-BE-V5 vitrimer: 30 min of creep under a stress of 0.1 MPa followed by 30 min of recovery at 40 °C.
Figure S22. Consecutive elongational creep-recovery experiments for PB-BE-V7 vitrimer: 30 min of creep under a stress of 0.1 MPa followed by 30 min of recovery at 60 °C.

Figure S23. Step-stress elongational creep-recovery (consecutive cycles of 30 min of creep under a load of 0.01 MPa followed by 30 min of recovery; 5th cycle presented) at different temperatures for PB-BE-V3 vitrimer.
Table S1. Viscosities of vitrimers calculated from the fifth cycle of consecutive step stress creep-recovery experiments.

<table>
<thead>
<tr>
<th></th>
<th>PB-BE-V3</th>
<th>PB-BE-V5</th>
<th>PB-BE-V7</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>η (Pa.s)</td>
<td>η (Pa.s)</td>
<td>η (Pa.s)</td>
</tr>
<tr>
<td>40</td>
<td>2.0 × 10⁹</td>
<td>4.8 × 10¹⁰</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>1.0 × 10⁹</td>
<td>2.4 × 10¹⁰</td>
<td>1.3 × 10¹¹</td>
</tr>
<tr>
<td>80</td>
<td>7.9 × 10⁸</td>
<td>1.4 × 10¹⁰</td>
<td>6.5 × 10¹⁰</td>
</tr>
<tr>
<td>100</td>
<td>6.3 × 10⁸</td>
<td>6.6 × 10⁹</td>
<td>2.5 × 10¹⁰</td>
</tr>
<tr>
<td>120</td>
<td>3.5 × 10⁸</td>
<td>2.7 × 10⁹</td>
<td>8.8 × 10⁹</td>
</tr>
</tbody>
</table>

Figure S24. Plots of log(η) (left) and log (τ) (right) versus 1000/T for PB-BE-V3 (green), PB-BE-V5 (red) and PB-BE-V7 (blue) experimental points (squares) and linear fits (solid lines) to extract the activation energy from the slope and $T_v$ from the abscissa at which log(η)=12 (dashed lines). Viscosities were extracted from stress step-stress creep data with Equation 1. Relaxation times were extracted from step-stress creep data with Equation 2.

Table S2. Summary of activation energies and $T_v$'s of vitrimers extracted from step stress creep-recovery experiments.

<table>
<thead>
<tr>
<th></th>
<th>PB-BE-V3</th>
<th>PB-BE-V5</th>
<th>PB-BE-V7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ/mol) from η</td>
<td>19.4</td>
<td>36.2</td>
<td>45.9</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol) from τ</td>
<td>20.5</td>
<td>36.0</td>
<td>49.3</td>
</tr>
<tr>
<td>$T_v$ (°C)</td>
<td>-98</td>
<td>-14</td>
<td>28</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>-12</td>
<td>1</td>
<td>15</td>
</tr>
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</table>
5) Dual networks

1. Creep and stress relaxation experiments

![Image of creep experiment graph]

**Figure S25.** Creep experiment at 30 °C and 0.1 MPa for **DN-HDT-3-BE-3, DN-HDT-4-BE-2** dual networks, **PB-BE-V5** vitrimer, and **PB-HDT-5** static network.

![Image of stress relaxation graph]

**Figure S26.** Stress relaxation of the dual network **DN-HDT-3-BE-3** at various temperatures and of the static network **PB-HDT-5** at 120 °C.
2. Mechanical properties of **DN-HDT-3-BE-3** and **DN-HDT-4-BE-2**

![Bar chart showing Young's modulus of different networks](image)

**Figure S27.** Young’s modulus at 25 °C of **PB-HDT-5** (gray) static network, **PB-BE-V5** (red) vitrimer, **DN-HDT-3-BE-3** (blue) and **DN-HDT-4-BE-2** (cyan) dual networks.

![Diagram showing storage modulus and tan delta](image)

**Figure S28.** Storage modulus and tan delta of **DN-HDT-3-BE-3** dual network before and after recycling.
Figure S29. Lap-shear test curves for dual networks lap joints prepared at 150 °C for 2 min. Crosshead speed is 10 mm/min. Results on multiple specimens (N = 3 specimens tested) are shown for reproducibility. The lap joints all broke via bulk fracture.