Transformation of polyethylene into a vitrimer by nitroxide radical coupling of a bis-dioxaborolane

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Supporting Information

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

**Fig. S1** $^1$H NMR spectrum of TEMPO-BE in CDCl$_3$, in the presence of phenylhydrazine.

**Fig. S2** $^{13}$C NMR spectrum of TEMPO-BE in CDCl$_3$, in the presence of phenylhydrazine.
Fig. S3 $^1$H NMR spectrum of Bis-TEMPO-BE in CDCl$_3$, in the presence of phenylhydrazine.

Fig. S4 $^{13}$C NMR spectrum of Bis-TEMPO-BE in CDCl$_3$, in the presence of phenylhydrazine.
2. Grafting characterization by FTIR spectroscopy

Fig. S5 FTIR spectra of HDPE, TEMPO-BE grafting agent and physical mixtures of HDPE with varying amounts of TEMPO-BE.

![FTIR spectra of HDPE, TEMPO-BE grafting agent and physical mixtures of HDPE with varying amounts of TEMPO-BE.]

Fig. S6 FTIR intensity of B-O (1359 cm\(^{-1}\)) (blue) and B-C (1100 cm\(^{-1}\)) (red) vibration bands of TEMPO-BE as a function of the molar ratio of TEMPO-BE. Average on 3 samples.
Fig. S7 FTIR spectra of HDPE grafted with TEMPO-BE: PE-G1, PE-G2, PE-G3 and PE-G4.

Fig. S8 FTIR spectra of HDPE grafted with TEMPO-BE: PE-G1, PE-G2, PE-G3 and PE-G4.

The degree of functionalization of grafted HDPE was calculated using the equations provided in Fig. S6 and normalizing the C-H bending vibration (1470 cm$^{-1}$) of PE to an intensity of 1.
Fig. S9 FTIR spectra of the insoluble part of PE-V1 and PE-V2.

The degree of functionalization of HDPE vitrimers was calculated using the equations provided in Fig. S6 and normalizing the C-H bending vibration (1470 cm$^{-1}$) of PE to an intensity of 1.

3. Photographs of HDPE, PE-V1 and PE-V2

Fig. S10 Photographs of HDPE, PE-V1 and PE-V2. Scale in cm on the right.
4. Quantification of the degree of crystallinity by DSC

![Graph showing DSC of HDPE, PE-V1, and PE-V2](image)

Fig. S11 DSC of HDPE, PE-V1 and PE-V2.

<table>
<thead>
<tr>
<th></th>
<th>Melting point (°C)</th>
<th>Melting enthalpy (J/g)</th>
<th>Degree of crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>128</td>
<td>185</td>
<td>64.2</td>
</tr>
<tr>
<td>PE-V1</td>
<td>127</td>
<td>151</td>
<td>52.4</td>
</tr>
<tr>
<td>PE-V2</td>
<td>124</td>
<td>127</td>
<td>44.1</td>
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</tbody>
</table>

Table S1 Melting point and degree of crystallinity of HDPE, PE-V1 and PE-V2 determined by DSC.

The degree of crystallinity \( \chi_c \) was calculated from the specific enthalpy of melting \( \Delta H_m \) as \( \chi_c = \Delta H_m / \Delta H_m^* \), where \( \Delta H_m^* = 288 \, \text{J.g}^{-1} \) corresponds to the specific enthalpy of melting of a fully crystalline polyethylene.
5. **Stress relaxation on PE-V1 and zero shear viscosities of HDPE, PE-V1 and PE-V2**

![Normalized stress relaxation profiles (1% strain) of PE-V1 at different temperatures.](image)

**Fig. S12** Normalized stress relaxation profiles (1% strain) of PE-V1 at different temperatures.

**Table S2** Zero shear viscosities of HDPE, PE-V1 and PE-V2 vitrimers calculated from stress relaxation experiments

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$\eta_0$ (Pa.s)</th>
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</thead>
<tbody>
<tr>
<td>160</td>
<td>-</td>
<td>3.69 x 10^6</td>
<td>2.23 x 10^7</td>
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<tr>
<td>170</td>
<td>1.20 x 10^4</td>
<td>4.27 x 10^6</td>
<td>1.66 x 10^7</td>
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<tr>
<td>180</td>
<td>-</td>
<td>3.96 x 10^6</td>
<td>1.33 x 10^7</td>
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<tr>
<td>190</td>
<td>8.42 x 10^3</td>
<td>3.35 x 10^6</td>
<td>8.77 x 10^6</td>
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<tr>
<td>200</td>
<td>-</td>
<td>5.35 x 10^5</td>
<td>3.41 x 10^6</td>
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<tr>
<td>210</td>
<td>6.14 x 10^3</td>
<td>4.19 x 10^4</td>
<td>1.01 x 10^6</td>
</tr>
<tr>
<td>220</td>
<td>-</td>
<td>1.74 x 10^4</td>
<td>2.54 x 10^4</td>
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<tr>
<td>230</td>
<td>4.73 x 10^3</td>
<td>8.79 x 10^3</td>
<td>-</td>
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</tbody>
</table>
6. FTIR characterization of PE-V1 and PE-V2 after annealing at 250 °C

**Fig. S13** FTIR spectra of PE-V1 as extruded (black), of the insoluble part PE-V1 (green), of the insoluble part of PE-V1 after thermal annealing at 150 °C (yellow) and of PE-V1 after a thermal annealing at 250 °C followed by precipitation (red).

**Fig. S14** FTIR spectra of PE-V2 as extruded (black), of the insoluble part PE-V2 (green) and of PE-V2 after a thermal annealing at 250 °C followed by precipitation (red).
7. Strain sweep experiments on PE-V1 and PE-V2

Fig. S15 Variation of storage and loss modulus of PE-V2 at different temperatures with strain amplitude under an angular frequency of 1 rad.s⁻¹.

Fig. S16 Variation of storage and loss modulus of PE-V1 at different temperatures with strain amplitude under an angular frequency of 1 rad.s⁻¹.
Fig. S17 Storage (triangle) and loss (square) modulus of PE-V1 before and after annealing at 220 °C as a function of temperature with an angular frequency of 1 rad.s^{-1} and a strain of 0.1%.

8. Mechanical properties of HDPE, PE-V1 and PE-V2

Fig. S18 Tensile stress-strain curves at RT for the HDPE precursor, PE-V1 and PE-V2.
Fig. S19  Tensile stress-strain curves at 80 °C for the HDPE precursor, PE-V1 and PE-V2.

Fig. S20  Elongational creep tests at 80 °C and 5 MPa for the HDPE precursor (in red), PE-V1 (blue) and PE-V2 (grey) vitrimers. Results on 4 specimens are shown for reproducibility.