**Figure S1.** $^1$H NMR spectrum of cis-polybutadiene rubber (cis-BR) used in the present study using Bruker at 600 MHz, and deuterated chloroform (CDCl$_3$) as a solvent.

**Figure S2.** Inverse gated decoupling $^{13}$C NMR spectrum of cis-polybutadiene rubber (cis-BR) used in the present study using Bruker at 150 MHz, and deuterated chloroform (CDCl$_3$) as a solvent. Inverse gated decoupling $^{13}$C NMR is suitable for quantitative analysis due to the suppression of NOE.
Table. S1 Assignments of the shift for cis-1, 4, trans-1, 4, and 1, 2-structure in \(^1\)H NMR spectrum and inverse gated decoupling \(^{13}\)C NMR spectrum.

<table>
<thead>
<tr>
<th>(^1)H NMR</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.98</td>
<td>1, 2-structure (d)</td>
</tr>
<tr>
<td>5.38</td>
<td>(cis-1, 4 + trans-1, 4) (a+b)</td>
</tr>
<tr>
<td>5.58</td>
<td>1, 2-structure (c)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(^{13})C NMR</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.41</td>
<td>(cis-1, 4) (k)</td>
</tr>
<tr>
<td>32.69</td>
<td>(trans-1, 4) (l)</td>
</tr>
</tbody>
</table>

The total molar content of 1, 2-structure and 1, 4-structure of cis-BR can be easily calculated using \(^1\)H NMR spectrum. The relative molar content of \(cis\)-1, 4 and \(trans\)-1, 4-structure is calculated using inverse gated decoupling \(^{13}\)C NMR spectrum.

For \(^1\)H NMR spectrum:

\[
C_{1,2-structure} = \frac{A_d/2}{A_{a+b} + A_e - A_d/2 + A_d/2} \times 100\%
\]

\[
C_{1,4-structure} = 100 - C_{1,2-structure}
\]

where \(A\) represents the integrated area.

For \(^{13}\)C NMR spectrum, the relative molar content of \(cis\)-1, 4 and \(trans\)-1, 4-structure are below:

\[
R_{cis-1,4} = \frac{A_k/2}{A_k/2 + A_l/2} \times 100\%
\]

\[
R_{trans-1,4} = 100 - R_{cis-1,4}
\]

So, the total molar content of \(cis\)-1, 4 and \(trans\)-1, 4-structure can be calculated:

\[
C_{cis-1,4} = R_{cis-1,4} \times C_{1,4-structure}
\]

\[
C_{trans-1,4} = R_{trans-1,4} \times C_{1,4-structure}
\]

In this study, the content of \(cis\)-1, 4, \(trans\)-1, 4, and 1, 2-structure are calculated as 94.5%, 2.3%, and 3.2%, respectively.
Figure S3. Temperature-dependent FTIR spectra of the cross-linking process of cis-BR from 50 °C to 220 °C in the region 3750–2750 cm$^{-1}$.