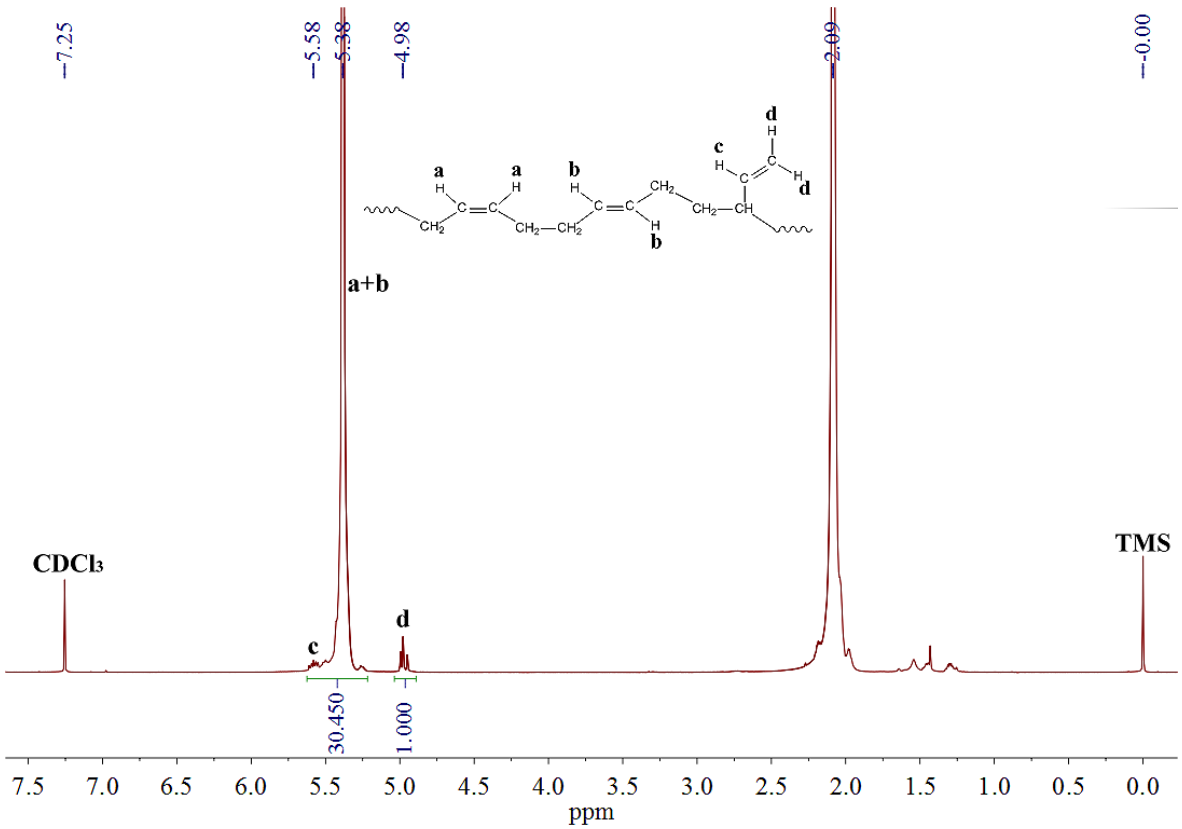

Figure S1. ^{1}H NMR spectrum of cis-polybutadiene rubber (cis-BR) used in the present study using Bruker at 600 MHz, and deuterated chloroform ($CDCl_3$) as a solvent.

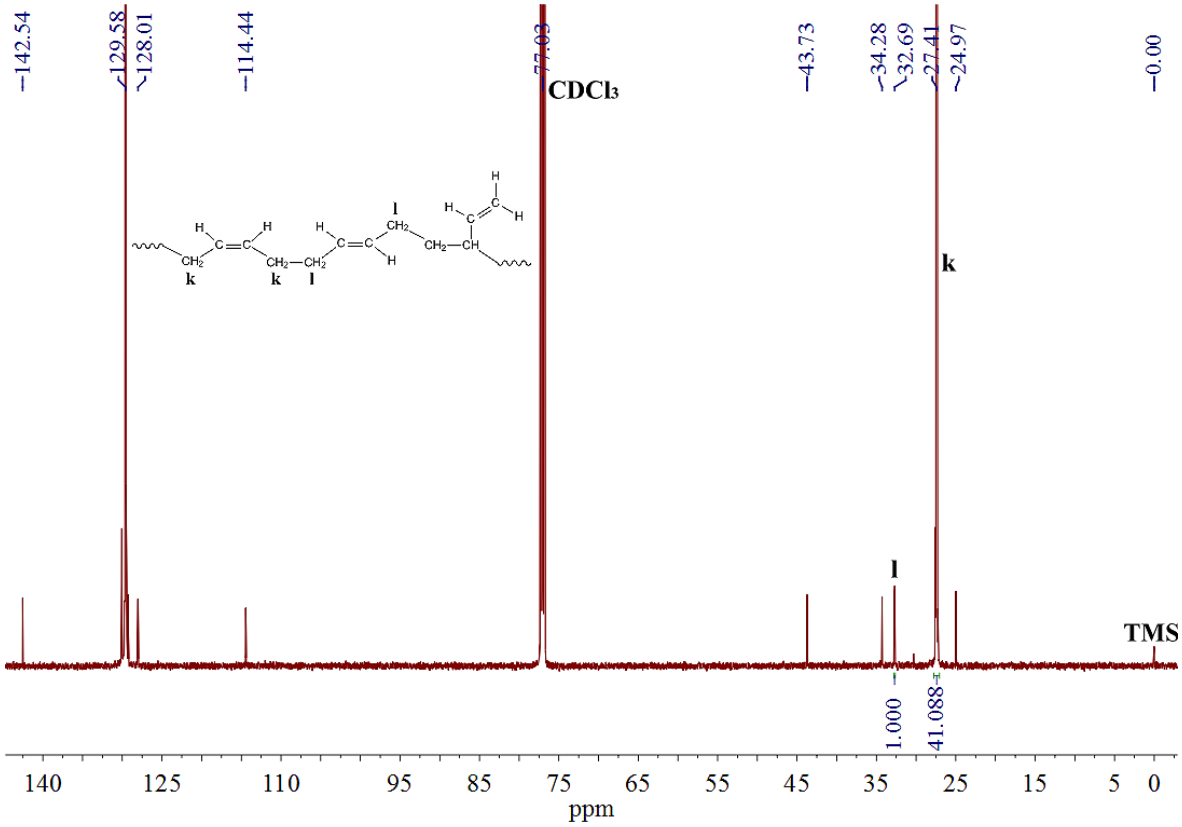

Figure S2. Inverse gated decoupling ^{13}C NMR spectrum of cis-polybutadiene rubber (cis-BR) used in the present study using Bruker at 150 MHz, and deuterated chloroform ($CDCl_3$) as a solvent. Inverse gated decoupling ^{13}C NMR is suitable for quantitative analysis due to the suppression of NOE.

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.

^{1}H NMR	
Shift (ppm)	**Assignments**
4.98	1, 2-structure (**d)**
5.38	*cis*-1, 4 + *trans*-1, 4 (**a**+**b)**
5.58	1, 2-structure (**c)**
^{13}C NMR	
Shift (ppm)	**Assignments**
27.41	*cis*-1, 4 (**k)**
32.69	*trans*-1, 4 (**l)**

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:

$$C_{1,\,2\text{-structure}} = \frac{A_d/2}{\frac{A_{a+b}+A_c-A_d/2}{2}+A_d/2}\times 100\%$$

$$C_{1,\,4\text{-structure}} = 100 - C_{1,\,2\text{-structure}}$$

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:

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

$$R_{\text{trans-1, 4}} = 100 - R_{cis-1,4}$$

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

$$C_{\text{cis-1, 4}} = R_{\text{cis-1, 4}} \times C_{1,4-structure}$$

$$C_{\text{trans-1, 4}} = R_{\text{trans-1, 4}} \times C_{1,4-structure}$$

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.

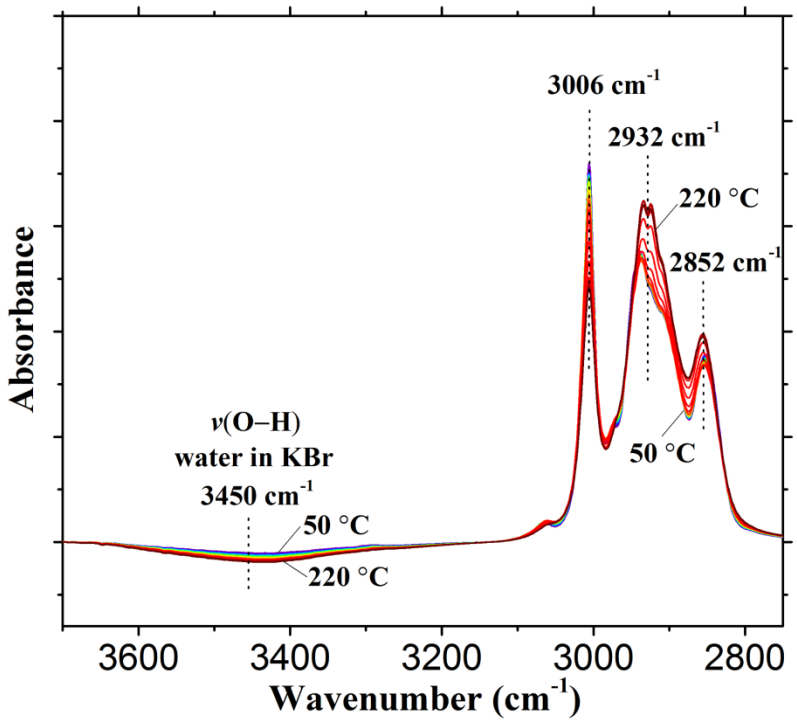

Figure S3. Temperature-dependent FTIR spectra of the cross-linking process of cis-BR from 50 °C to 220 °C in the region 3750−2750 cm^{-1}.