

1 Endow Rubber with Intrinsic Self-Healing Property Using Thiourea-Based 2 Polymer

3 Afreen Shagufta, ^{a,b,c,d} Lei Wang, ^{a,c,d} Senbiao Fang, ^{a,c,d} Qingshan Kong, ^{*a,c,d} and Haibo
4 Zhang ^{*a,c,d}

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6 ^aQingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences,
7 Qingdao 266101, China.

8 ^bUniversity of Chinese Academy of Sciences, Beijing 100049, China.

9 ^cQingdao New Energy Shandong Laboratory, Qingdao 266101, China.

10 ^dShandong Energy Institute, Qingdao 266101, China.

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12 *Corresponding authors: Haibo Zhang (zhanghb@qibebt.ac.cn); Qingshan Kong
13 (kongqs@qibebt.ac.cn).

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15 **This Supplementary file includes:**

16 **Synthesis of PTUEG₃**

17 **Figures S1, S2**

18 **Supporting table S1**

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20 **Synthesis of Thermoplastic polymer**

21 Initially, PTUEG₃ was synthesized following the procedure described in previous literature
22 with some modifications (Fig. S1).¹ Specifically, 1,2-bis(2-aminoethoxy)ethane (160 mg) and
23 1,1'-thiocarbonyl diimidazole (175 mg) were dissolved in a 50 ml solution of DMF. The
24 resulting mixture was stirred at 30 °C for 2 h, followed by additional stirring at 25 °C for 24
25 h. Subsequently, 50 ml of chloroform was added to the solution, and the diluted mixture was
26 poured into 1 L of diethyl ether for precipitation. The resulting precipitate was dissolved in
27 50 ml of chloroform, and the mixture was then re-precipitated in 1 L of diethyl ether to obtain
28 the purified product. The insoluble fraction was collected after centrifugation for 15 min at a
29 speed of 5000 rpm, yielding PTUEG₃ in the form of a shimmery yellow gel. This precipitate
30 was further dried in a vacuum oven at 140 °C for 12 h. The resulting yellow gel was then
31 cooled in a Teflon mold and processed to form a solid, transparent substance in a vacuum

32 oven at ambient temperature, resulting in a dry, solid polymer.

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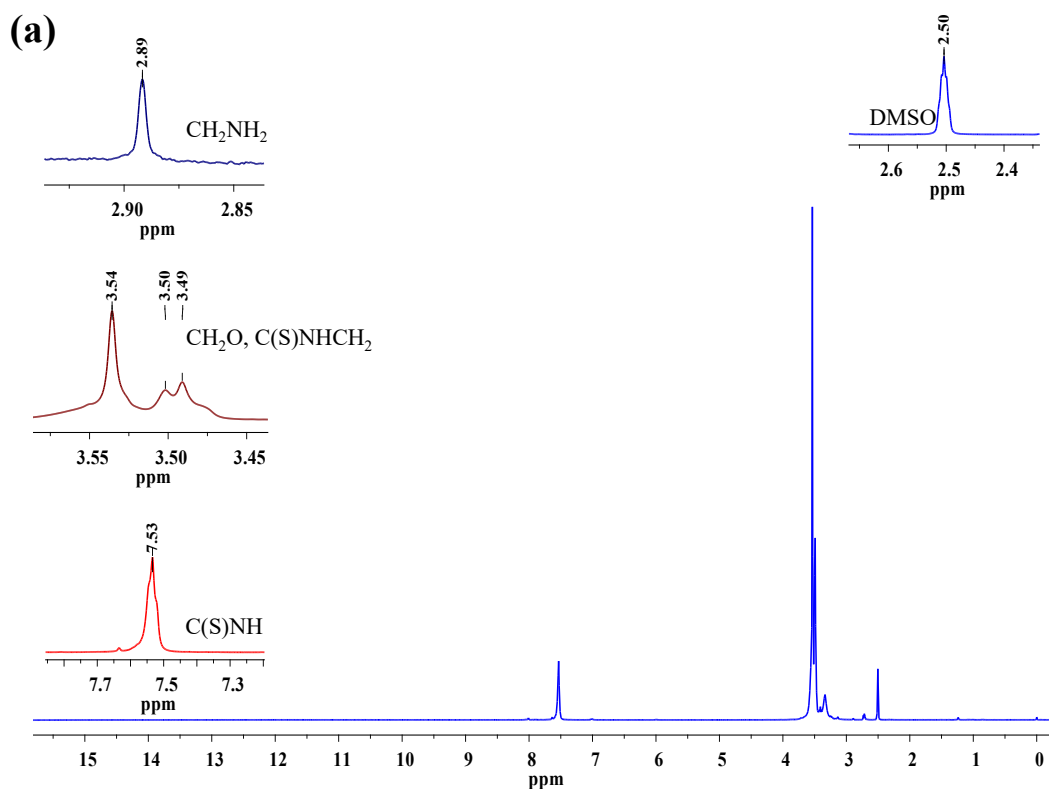
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Fig. S1 Schematic representations of synthesis PTUEG₃

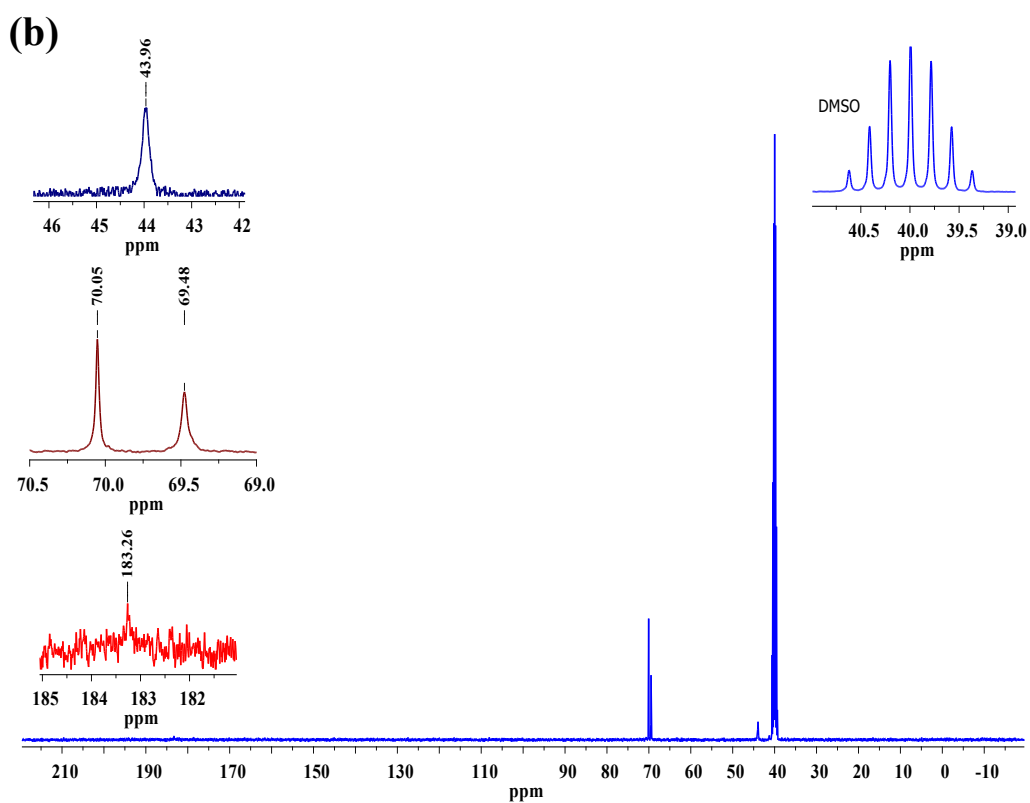
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37 NMR spectra

38 PTUEG₃ was produced as a thermoplastic polymer and was characterized using ¹H and ¹³C
39 nuclear magnetic resonance (NMR) spectroscopy. As shown in (Fig. S2a), ¹H NMR end-
40 group analysis at 500 MHz (DMSO-d₆) revealed multiple peak distributions of 2.89 (br,
41 CH₂NH₂), 3.49–3.54 (br, CH₂O, C(S) NHCH₂), and 7.53 (br, C(S) NH). However, a slight
42 shift of 0.05 ppm was observed, with the signal at 3.49 ppm shifting to a higher frequency at
43 3.54 ppm, attributed to the action of sulfur bonds. In (Fig. S2b), ¹³C NMR (125 MHz,
44 DMSO-d₆) showed peaks at 43.96, 69.48, 70.05 and 183.26 with a repeat delay of 10s. The
45 high concentration of the samples resulted in standard signal/noise ratios. The chemical shifts
46 (δ in ppm) were calculated using non-deuterated solvent residues. The average number of
47 repeating units was determined to be 50 based on the intensity ratio between the signals at δ
48 2.89 (2H br, CH₂NH₂) and 7.53 ppm (thiourea-H).



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51 Fig. S2 (a) ¹H and ¹³C (b) NMR spectra for PTUEG₃ (DMSO-d₆, 298K). The signals at δ 2.50
52 (¹H) and 39.5–40.5 ppm (¹³C) are partially non-deuterated residues of DMSO-d₆ and water.

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54 Supporting table

55 Table S1: Comparative study of self-healing rubber materials

Rubber material	Healing time (hrs)	Stimulation	Tensile strength (MPa)	Elongation at break (%)	References
ENR-CNCs	24	RT	1.19	500	2
WNRPs-PSR	24	100 °C	1.15	220	3
ENR-CMCS-PDA-B ⁻	24	60°C	1.64	777	4
SBR-BDB	24	80°C	2.68	200	5
ENR-t-CNs	24	RT	4.04	198	6
PBR-CuCl ₂	12	110 °C	4.0	530	7
SPB	12	RT	1.78	322	8
NR-MA-DGEBA	8	120 °C	1.2	250	9
SBR- C _{2,5} -GTR1	7	70°C	2.51	617	10
SBR-MWCNT-FA	5	100 °C	3.5	480	11
NR-g-MA	4	130 °C	1.47	325	12
ENR-CABt	3	150 °C	4.5	400	13
NR-ENR-PTUEG ₃	12	RT	4.83	833	This work

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57 Notes and references

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