Materials

4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy radical (4-OH-TEMPO, 98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. 2,4-Diisocyanate-1-methylbenzene (TDI, CR) was supplied by Sinopharm Chemical Reagent Co., Ltd. Toluene (99%) was purchased from Chengdu Kelong Chemicals Co., Ltd. Styrene–butadiene rubber (SBR 1502, 20.0% cis-1,4, 45.3% trans-1,4, 11.2% vinyl group and 23.5% combined styrene, M_n 7.3×10^4, M_w 33.5×10^4, M_w/M_n 4.6) was obtained from Jilin Chemical Co., Ltd.

Synthesis of reversible crosslinker

First, 19.780 g of 4-OH-TEMPO was completely dissolved in 30 mL of toluene in a 250-cc three-necked round-bottomed flask. After the flask was completely under nitrogen, 10 mL of TDI was slowly dropped in the above flask. (The molar ratio of the hydroxyl group to the isocyanate group was 1:1) The flask was placed in an oil bath at 80 °C and magnetically stirred for 8 h under nitrogen. The volatile solvents were evaporated using a rotary evaporator, affording a red, translucent solid. The product was isolated and purified by silica gel column chromatography. Finally, a reversible crosslinker with double nitroxides was obtained, defined as DTEMPO. Yield: 28.80 g (97%). Pinkish-orange solid. Mp 74 °C. ^{1}H-NMR (600 MHz, CDCl$_3$): δ 8.19 (d, 2H), 2.36 (s, 3H), 1.83 (m, 4H), 1.45 (m, 4H), 0.03-0.29 (d, 24H). HRMS (ES$^+$): m/z calcd for $C_{27}H_{42}N_4O_6{}^{2.}$ [(M + Na) $^+$], 541.2998; found, 541.3017. Elemental analysis % calc. (% found): C 62.53 (63.59), H 8.16 (7.96), N 10.80 (10.60), O 18.51 (17.85).

Preparation of thermoreversible rubber

First, 50 g of SBR was plasticized on the two-roll mill (25 °C) thrice, followed by the addition of a certain amount of DTEMPO to mix with SBR. After completely mixing within 10 min, the rubber compound was hot-pressed on a plate vulcanizer (140 °C, 19 MPa) for 10 min. Table 1 lists the detailed formulation of all the SBR samples, expressed as parts per hundreds of rubber (phr). Finally, thermoreversible styrene-butadiene rubber crosslinked by DTEMPO was obtained, defined as DSBRy throughout the manuscript, where y is the content of DTEMPO (in phr) incorporated into the DSBR.

Table S1 The formulation of DSBRy

Sample	SBR/phr	DTEMPO/phr
DSBR5	100	5
DSBR8	100	8
DSBR10	100	10
DSBR12	100	12
DSBR15	100	15

Repeated processing of thermoreversible rubber

Firstly, DSBR was pre-heated on a 140 °C hot-mill for 5 min, followed by completely shearing. Second, it was hot-pressed on a plate vulcanizer at 140 °C for 10 min. Finally, reprocessed DSBR-x was obtained (x represented the number of successive reprocessing experiments, the first reprocessed product was DSBR-1st, the second reprocessed product was DSBR-2nd and the third reprocessed product was DSBR-3rd).

Preparation of the control rubber sample

Firstly, 100 phr of SBR was plasticized on the two-roll mill (25 °C) thrice, followed by the addition of 4.0 phr of zinc oxide, 2.0 phr of stearic acid, 0.5 phr of 2-mercaptobenzothiazole, 1.5 phr of N-cyclohexylbenzothiazole-2-sulphenamide and 1.5 phr of sulfur in that order and mixed uniformly. Second, the compound was hot-pressed on a plate vulcanizer at 150 °C for the maximum curing time. Finally, the control rubber sample (SBR-S) was prepared.

Characterizations

The Bruker Vector 33 Fourier transform infrared (FTIR) spectrometer was utilized to characterize 4-OH-TEMPO, TDI, DTEMPO, uncured DSBR and cured DSBR. Variable-temperature infrared spectra of cured DSBR were recorded. First, the sample was tested at 25 °C, followed by heating it up to 140 °C, then cooling it to 25 °C and heating it up to 140 °C again. IR spectra at different temperatures were recorded.

The ^{1}H NMR of DTEMPO was recorded on a Bruker AVANCE III HD 600 instrument using CDCl$_3$ as the solvent.

The high-resolution mass spectrum of DTEMPO was recorded on an Bruker Agilent1290 / maXis impact instrument which was operating in positive ion mode.

The elemental analysis for C, H and N were performed using a Elementar Vario EL cube elemental analyzer.

Glass transition temperatures of uncured DSBR and cured DSBR were measured on a TAQ20 differential scanning calorimeter by heating the samples from −80 °C to 25 °C at a rate of 10 °C/min under nitrogen.

Thermogravimetric analysis (TGA) was performed on a TAQ500 thermogravimetric analyser from 25 °C to 900 °C at a heating rate of 20 °C/min under nitrogen to characterize the thermal properties of DSBR-x.

Electron spin resonance (ESR) spectra were recorded on a Bruker A300-10-12 spectrometer equipped with a nitrogen and heating setup, operating at a modulation frequency of 100 kHz. Data acquisition was conducted at 25 °C and 140 °C and repeated thrice.

Rubber processing analysis (RPA 2000) from Alpha Technology Inc. was employed to characterize the variation in the modulus with temperature (60 °C–140 °C–60 °C–140 °C).

The Flory-Rehner equation[1] was used to calculate the crosslinking density (V_e) of SBR and DSBR-x, expressed as follows:

$$V_e = -\frac{1}{V}\left(\frac{Ln(1-V_2) + V_2 + \chi V_2^2}{V_2^{1/3}}\right)$$

(1)

where V_2 represents the volume fraction of the rubber phase in the swelling vulcanizate. The χ value represented the interaction parameters of rubber and the solvent, which was assumed to be 0.0653 for the SBR–toluene system. V represents the molar volume of toluene (106 cm³/mol). V_2 was calculated as follows:

$$V_2 = V_1 / (V_1 + V_s)$$

(2)

$$V_s = (M_2 - M_1) / \rho_s$$

(3)

$$V_1 = M_3 / \rho$$

(4)

where V_1 represents the volume of the rubber phase, and V_s represents the volume of the solvent in rubber after swelling. ρ_s represents the density of the solvent (0.866 g/cm³), and ρ represents the density of rubber. M_1 represents the mass of the vulcanizate before swelling, and M_2 represents the mass of the vulcanizate after swelling for 24 h. M_3 represents the mass of the swelling rubber after drying at 60 °C for 24 h under vacuum.

Approximately 100mg of each DSBR sample before and after crosslinking, respectively, was immersed in toluene at room temperature for 72 h. Toluene was replaced every 24 h. The solvent was decanted and the swollen samples were dried in a vacuum oven at 80 °C until constant weight. The sol fraction was calculated as follows:

$$Sol\ fraction = (M_0 - M_f) / M_0 \times 100\%$$

(5)

where M_0 represents the mass of the sample before the sol fraction experiment and M_f represents the mass of the dried sample.

Tensile tests were performed on dumbbell-shaped specimens according to ISO 37 with a tensile rate of 500 mm/min on a ZWICK universal testing machine at room temperature. Tear tests were performed on angular splines according to ISO 34-1 on a ZWICK universal testing machine.

Resilience test was conducted on a GOtech GT-7042-RE rubber resilience testing machine according to ISO 4662 under ambient conditions.

Dynamic mechanical analysis (DMA) was conducted on a NETZSCH DMA242C dynamic thermomechanical analyser under 1 Hz at a heating rate of 1 °C/min in nitrogen. The molecular weight between crosslinks of thermoreversible DSBR, Mc, was calculated as follows:[2]

$$M_c = 3(1 - 2/\emptyset)\rho RT / E'$$

(6)

where E' represents the storage modulus in the rubbery plateau zone, ρ, R, T and $\emptyset$ represent the density, gas constant, absolute temperature and functionality of the crosslinking site, respectively. In this study, E' values at T = T_g+30 °C were applied in the equation.
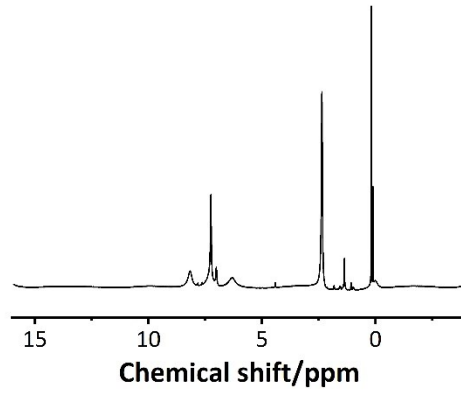
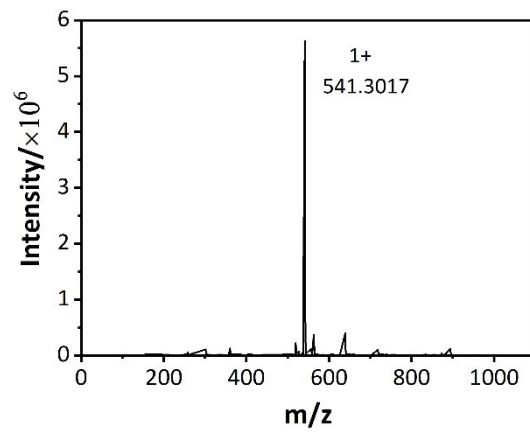**Fig. S1** ^{1}H-NMR spectrum of DTEMPO.
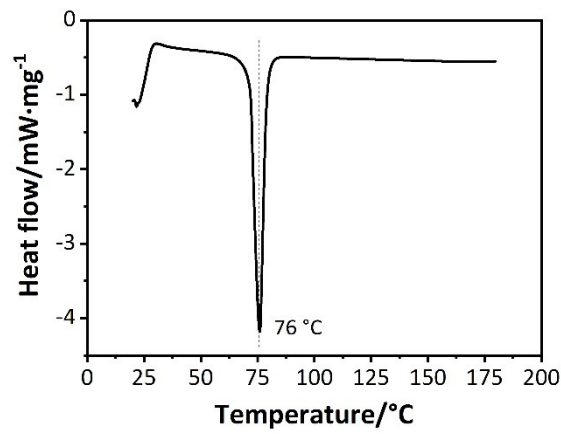

Fig. S2 High-resolution mass spectrum of DTEMPO.

Fig. S3 DSC curve of DTEMPO.
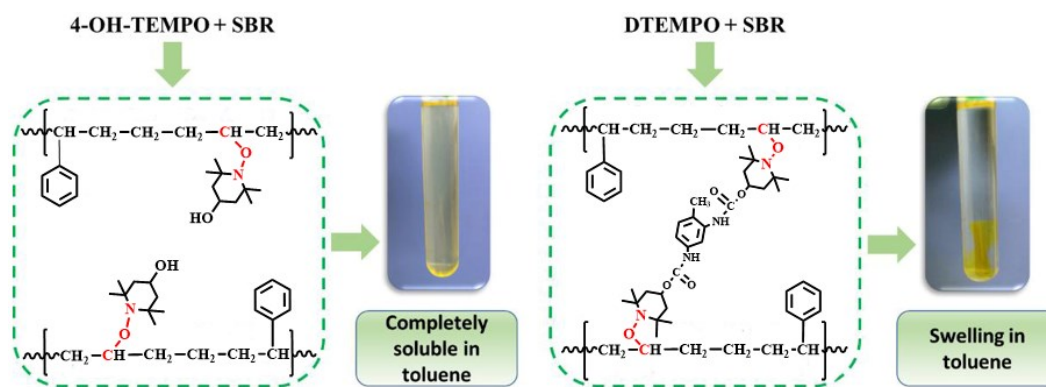
Fig. S4 Dissolution-swelling experiment of TSBR and DSBR.

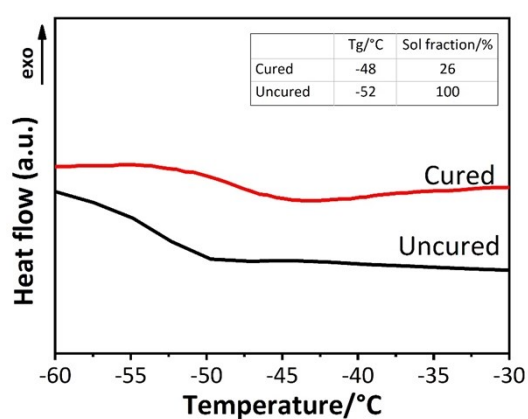|	Tg/°C	Sol fraction/%
Cured	-48	26
Uncured	-52	100

Fig. S5 DSC curves and sol fractions of uncured and cured DSBR.
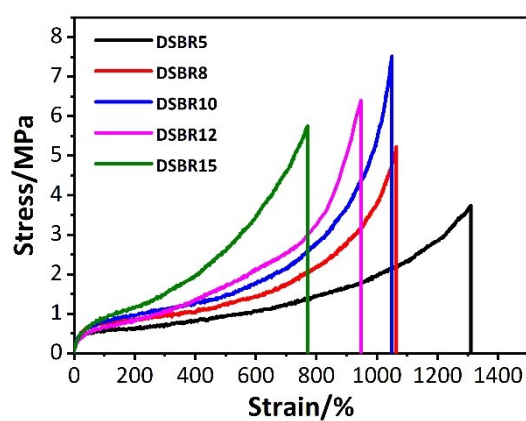

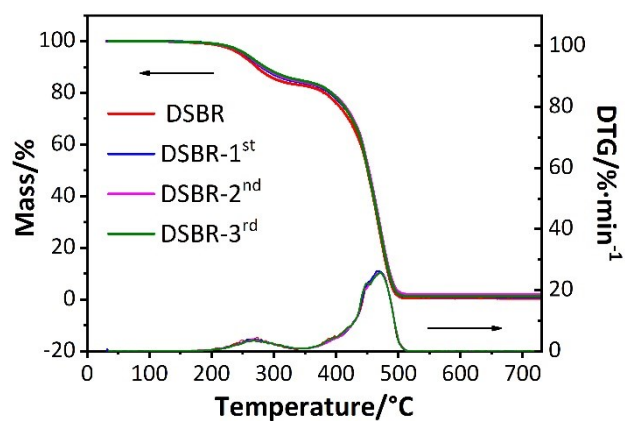**Fig. S6** Stress-Strain curves of DSBRy.

Fig. S7 TG and DTG curves of DSBR10 after reprocessing.

Table S2 Mechanical properties of DSBR and DSBR-1st, 2nd and 3rd

	Tensile strength /MPa	σ	Strain-at-break /%	σ	Tear-A /kN·m^{-1}	Permanent set/%	Crosslinking density V_e/× 10^{-5} mol·cm^{-3}
DSBR	7.46±0.19	0.14	1057±22	17	13.21±0.22	28	7.69±0.21
DSBR-1st	7.59±0.15	0.12	1054±16	13	15.54±0.45	20	7.52±0.10
DSBR-2nd	7.41±0.05	0.05	1048±28	25	16.60±0.12	24	7.17±0.33
DSBR-3rd	7.40±0.13	0.11	1010±34	31	14.73±0.08	20	7.83±0.15

Table S3 Molecular weight between crosslinks, Mc, of DSBR under different cycles.

Sample	E' at T_g + 30°C/MPa	M_c/g·mol^{-1}
DSBR-1st	4.16	523
DSBR-2nd	3.79	575
DSBR-3rd	3.54	615

1   O. Lorenz and C. R. Parks, *J. Polym. Sci.*, 1961, **50**, 299-312.
2   M b. J. He, W. X. Chen and X. X. Dong, *Polymer Physics*, Fudan University Press, Shanghai, 2nd edn,2000.