

Electronic Supporting Information

Correlation between Stress Relaxation Dynamics and Thermochemistry for Covalent Adaptive Networks Polymer

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Materials. The styrene-butadiene rubber (SBR) was kindly provided by Yanshan Branch, SINOPEC Beijing Research Institute of Chemical Industry. The SBR dry copolymer contains 26 wt % styrene (15 mol %) and 74 wt % butadiene (ca. 35 mol % 1, 4 units and ca. 50 mol % vinyl units), with an average molecular weight (M_n) of 53400 g mol⁻¹. Furfuryl mercaptan (FS), α , α' -azobisisobutyronitrile (AIBN), bismaleimide (M_2) were purchased from Adamas. Antioxidant (Ciba IRGANOX 1098) was obtained from BASF. M_2 was recrystallized in a mixed solvent of dichloromethane and hexane (2/1, v/v). Toluene was purified by standard procedures before use. All the other analytical grade reagents were purchased from Beijing Chemical Reagents Corp. and used as received.

Chemical Modification of SBR with Furfuryl Mercaptan. Furanfuryl modified styrene-butadiene rubber (SBR-FS) was synthesized as previously reported.¹ Briefly, SBR (20 g), furfuryl mercaptan (18.52 ml) and AIBN (0.533 g) were fully dissolved in 200 ml dry toluene. After backfilling the flask with nitrogen for three times, the solution was heated under stirring at 90 °C for 4~5 hrs. Then, the product was precipitated by pouring the solution into ethanol followed by repeatedly dissolving in dichloromethane and re-precipitation in ethanol for 5 times, and then kept at 60 °C under vacuum over 24 hrs to give viscous SBR-FS with a yield of 99 %. The degree of furan substitution (DS) (mole fraction relative to the total number of monomer units) along the SBR backbone was calculated from the ¹H NMR spectra according to the following equation:

$$DS(\%) = \frac{A_{\delta=3.68}}{A_{\delta=4.95} + A_{\delta=3.68}} \times 50\% \quad (S1)$$

where $A_{\delta=3.68}$ and $A_{\delta=4.95}$ represent the integral areas of the ethyl protons in grafted furfuryl group and vinyl double bonds, respectively.

Preparation of the CANs Films. The Covalent Adaptive Networks (CANs) elastomers were prepared by solvent-casting method. The solution containing SBR-FS, bismaleimide (M_2) and 0.1 wt % of antioxidant in dichloromethane was cast onto Teflon sheet and dried in the air and then in vacuum oven at 60 °C overnight. SBR-FS/ M_2 films with a thickness of ca. 0.2 mm were hot-compressed at 145 °C under 9 MPa. The films were then annealed at 70 °C for 3 hrs and stored at room temperature over 24 hrs before testing. Several samples with different molar ratios of furan/maleimide moieties (F/M=2/1, 4/1 and 10/1) were prepared, and the cross-linked samples with F/M = $x/1$ is denoted as x F-M.

Measurements. Nuclear magnetic resonance (NMR) spectra were measured at ambient temperature using $CDCl_3$ as a solvent on a 400 MHz, Bruker Avance spectrometer. Thermal analysis was carried out on a TA Q2000 differential scanning calorimeter at a heating/cooling rate of 10 °C min^{-1} . Dynamic mechanical thermal analysis (DMTA) was carried out on a TA Instruments Q800 with film tension clamps under the temperature range from -40 to 130 °C. The rectangular specimens with approximately dimension of 6 mm \times 4 mm \times 0.2 mm were tested at a heating rate of 3 °C min^{-1} . The oscillation frequency and oscillation amplitude were 1 Hz and 20 μm , respectively. A preload force of 0.001 N and a force track factor of 125 % were used.

Fourier transform infrared spectra (FTIR) were recorded on a Thermo Scientific Nicolet 6700 spectrometer by signal averaging 16 scans at a resolution of 4 cm^{-1} . In-situ FTIR measurement was carried out by using a Linkam FTIR 600 hot-stage under nitrogen atmosphere in transmission mode.

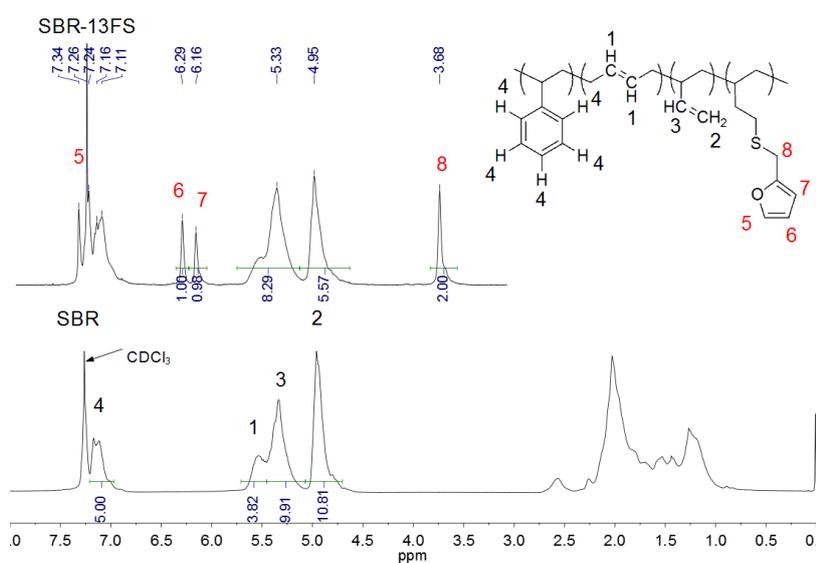
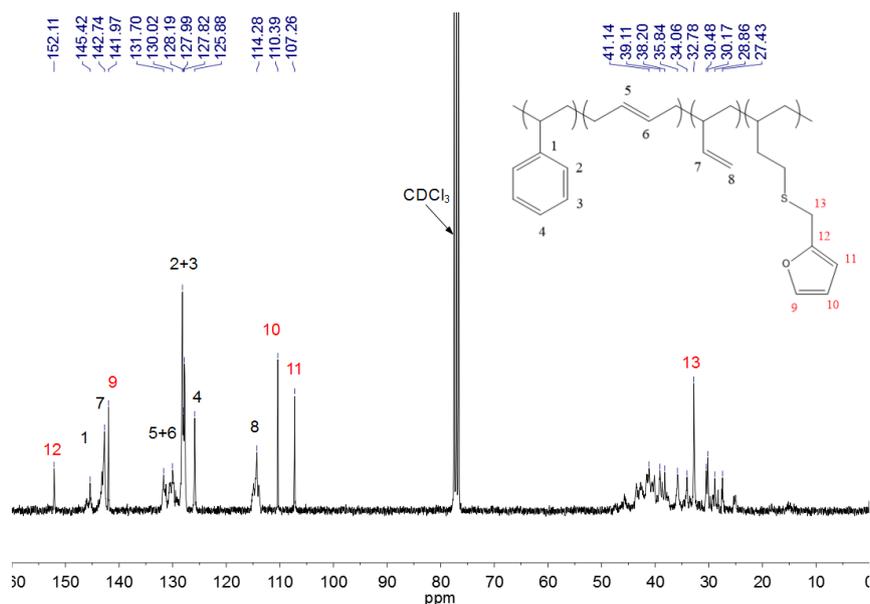
Tensile stress-relaxation experiments of the cross-linked elastomers were performed on a DMA Q800 instrument. The rectangular films were firstly preloaded by a 0.001 N force to ensure straightness. After reaching the testing temperature, the samples were allowed 30 min for the reaction equilibrium, and then stretched to 3 % strain and the deformation was maintained during the test. The 10F-M samples were deformed with a 5 % strain. The decrease of stress was recorded and the stress relaxation modulus was calculated and further normalized by the initial modulus.

Table S1 Parameters of SBR and SBR-FS samples

Sample	$DS^a(\%)$	M_n^b ($10^3\text{g}\cdot\text{mol}^{-1}$)	M_w^b ($10^3\text{g}\cdot\text{mol}^{-1}$)	PDI^b	$T_g^c(^\circ\text{C})$
SBR	0	53.4	56.1	1.05	-25.2
SBR-13FS	13.2	66.3	70.2	1.06	-15.9

^a Determined by ^1H NMR spectra. ^b Determined by GPC using PS as a standard.

^c Measured by DSC at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

**Fig. S1** ^1H NMR spectra of pristine SBR and SBR-FS samples.**Fig. S2** ^{13}C NMR spectrum of SBR-FS sample.

For the non-diffusion controlled regime, a simple model assuming a second order reaction for the forward reaction and first order behavior for the retro-reaction can be expected to describe DA/rDA kinetics.² The sample after complete DA reaction was utilized to test the rDA reaction kinetics at evaluated temperature. The rate of consumption of adduct, $d[A]/dt$ is then given as :

$$-\frac{d[A]}{dt} = \frac{d[M]}{dt} = \frac{d[F]}{dt} = k_f[A] - k_r[M][F] \quad (S2)$$

where k_f and k_r are the forward and reverse rate constants, respectively, and $[F]$, $[M]$, and $[A]$ the concentrations of furan, maleimide, and the adduct, respectively. The stoichiometric ratio of maleimide to furan moieties is r . Applying the definition of adduct conversion (p), $[A] = [A]_0(1-p)$, $[M] = [A]_0 p$, $[F] = [A]_0(r^{-1}-1+p)$, gives,

$$\frac{dp}{dt} = k_f(1-p) - k_r[A]_0 p(r^{-1}-1+p) \quad (S3)$$

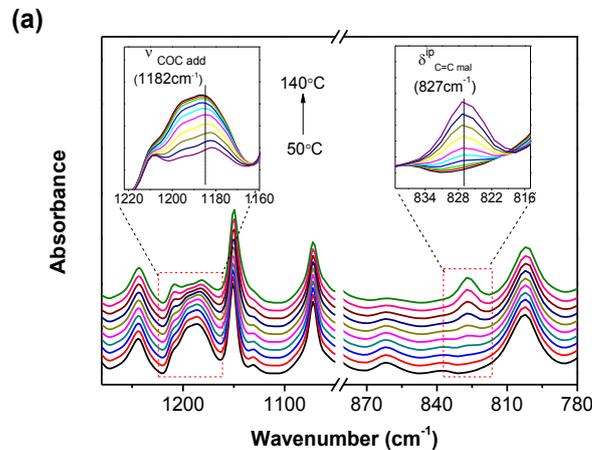
When $r=0.1$, i.e., $r^{-1} \gg 1$, we get $r^{-1}-1+p \approx 9$ for all the conversion data.

Eq. S3 can be simplified as,

$$\frac{dp}{dt} = k_r - (k_r + 9k_f[A]_0)p \quad (S4)$$

The integration of eq. S4 gives the conversion:

$$p = \frac{k_r - \exp[-(k_r + 9k_f[A]_0)t]}{(k_r + 9k_f[A]_0)} \quad (S5)$$



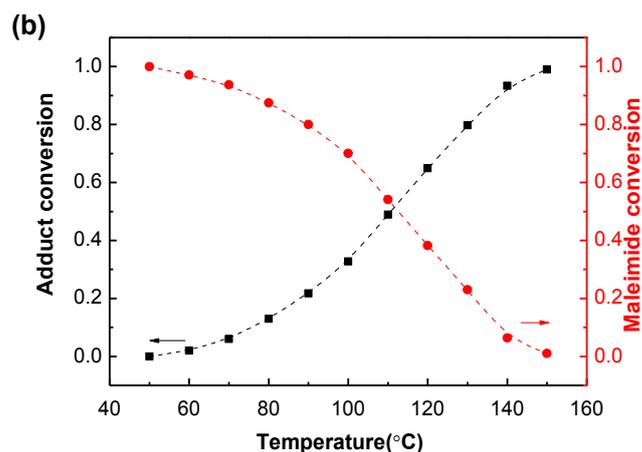


Fig. S3 (a) In-situ FTIR spectra of 10F-M samples during heating process from 50 to 140 °C with interval of 10 °C. Inserted was the absorbance of maleimide at 827cm^{-1} (C=C deformation) and adduct at 1182cm^{-1} (C-O-C stretching) (b) The evolution of adduct and maleimide conversion as a function of temperature for 10F-M by following the band of 827cm^{-1} and 1182cm^{-1} , respectively. Each measurement was tested at a specific temperature after the reaction equilibrium was obtained.

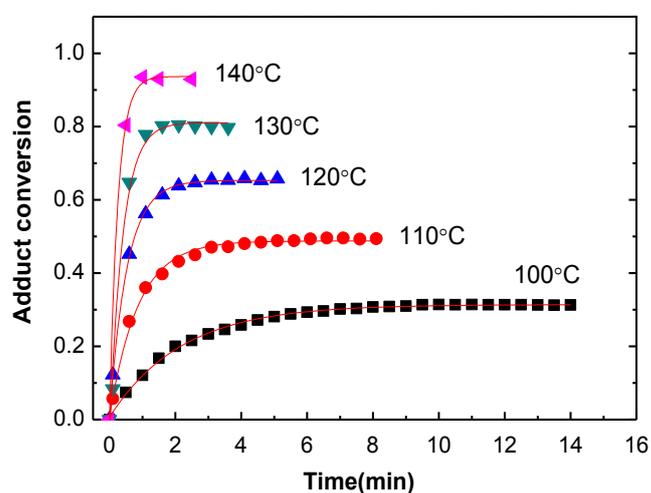


Fig. S4 Plot of the adduct conversion versus time, lines represent fits to eq. S5. Isothermal tests were measured at 100~140 °C with the interval of 10 °C.

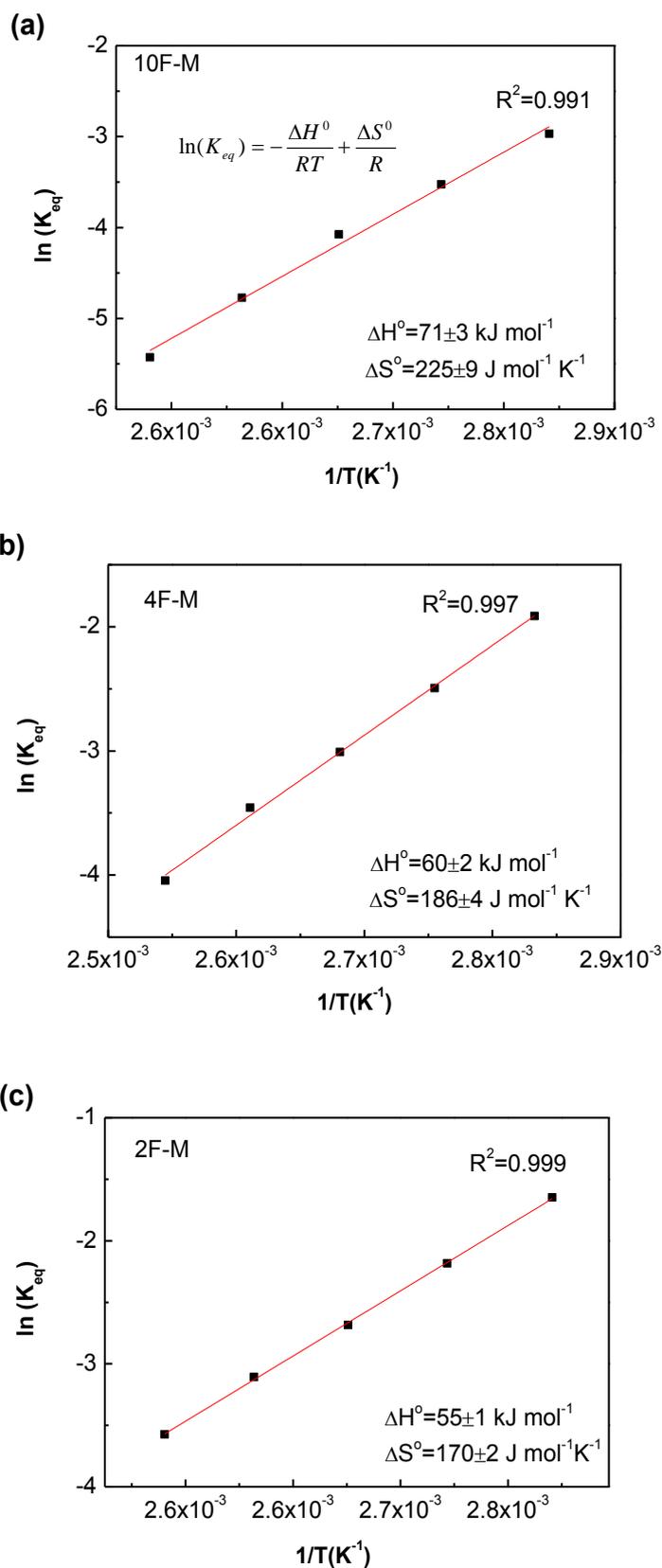


Fig. S5 Van't Hoff plots to determine the enthalpy of reaction (ΔH_r°) and entropy of reaction (ΔS_r°) for CANs elastomers: (a) 10F-M, (b) 4F-M, and (c) 2F-M.

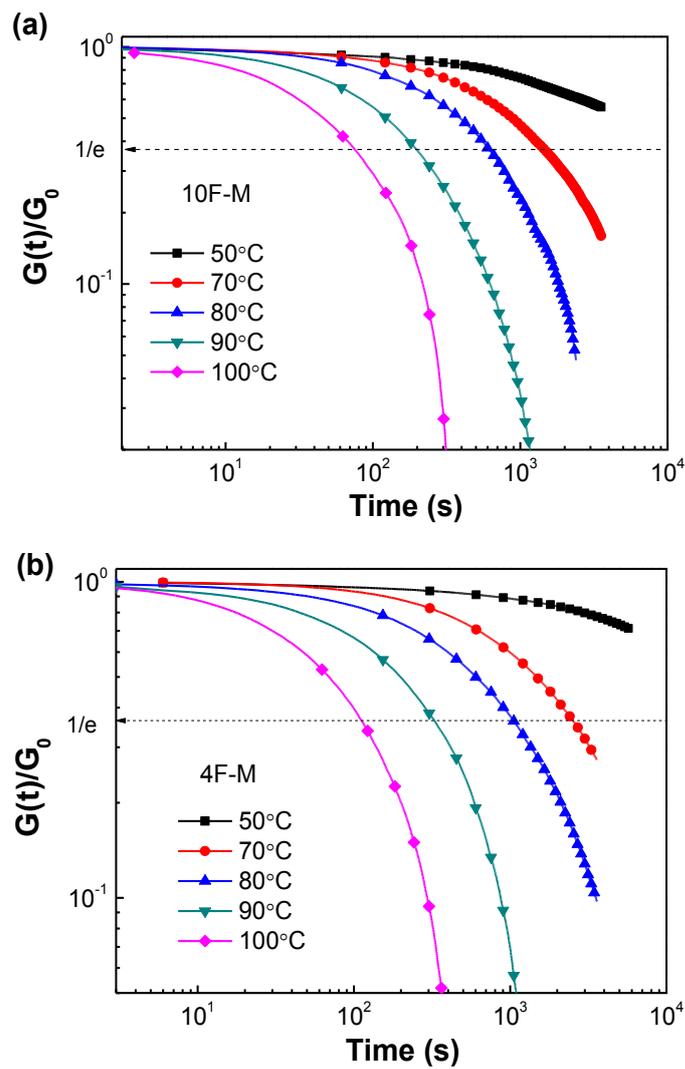


Fig. S6 Normalized stress relaxation curves of CANs elastomers at different temperatures: (a) 10F-M, (b) 4F-M.

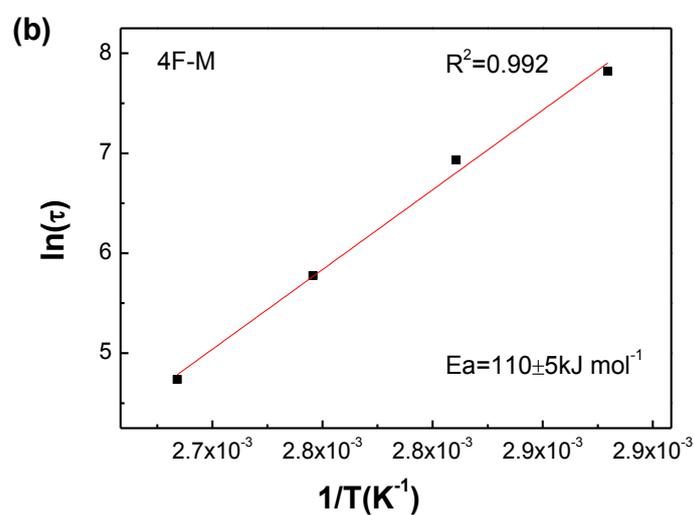
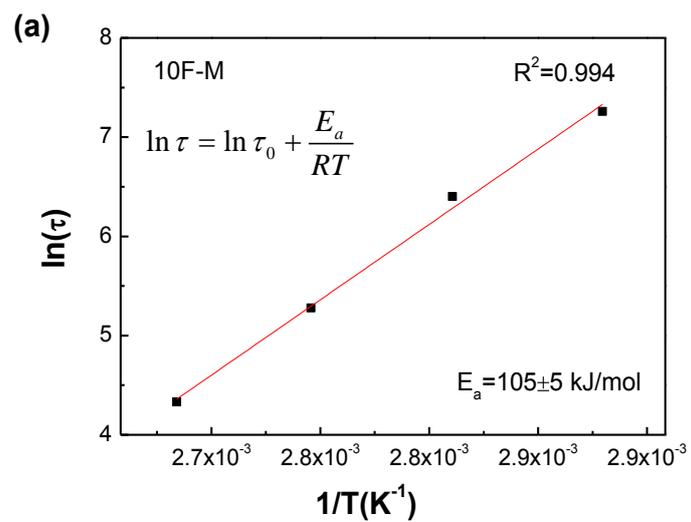


Fig. S7 Fitting of the relaxation times of CANs elastomers to the Arrhenius' equation:

(a) 10F-M, (b) 4F-M.

$$\ln(\alpha_T) = \ln\left(\frac{\tau}{\tau_r}\right) = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_r}\right) \quad (\text{S6})$$

where α_T is the shift factor, τ is the stress relaxation time, τ_r is the stress relaxation time of reference sample and temperature, E_a is the activation energy of relaxation, T is the absolute temperature and T_r is the reference temperature.

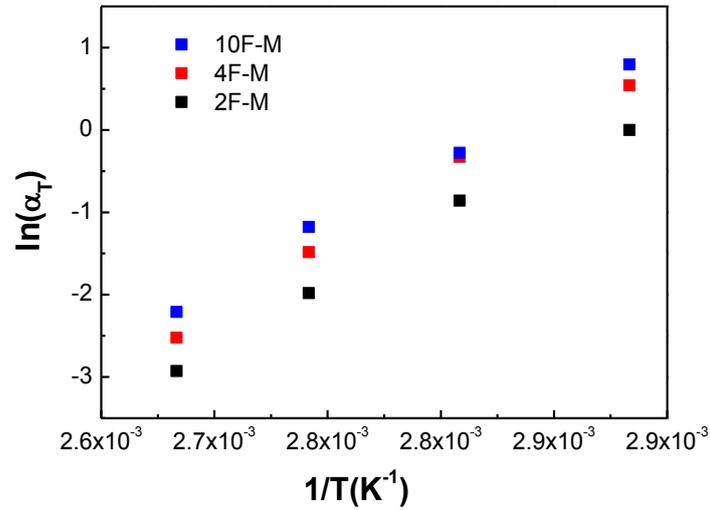


Fig. S8 Shift factors plotted as a function of inverse temperature. The shift factor was calculated with the reference of 10F-M sample at 70 °C.

Reference

- 1 X. Kuang, G. Liu, X. Dong and D. Wang, *Macromol. Mater. Eng.* 2016, **301**, 535.
- 2 R. J. Sheridan and C. N. Bowman, *Macromolecules* 2012, **45**, 7634.