

Supplementary information

Designing Dual-Domain Thermoplastic Elastomers from ABA Triblock Copolymers: Introducing Bond-Exchangeable Subdomains in the B-Block Strands

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1. $^1\text{H-NMR}$

The synthesis of target polymers was confirmed by $^1\text{H-NMR}$ spectroscopy. Figure S1 represents the spectrum for SBS before chemical modifications, and the integral ratios are summarized in Table S1.

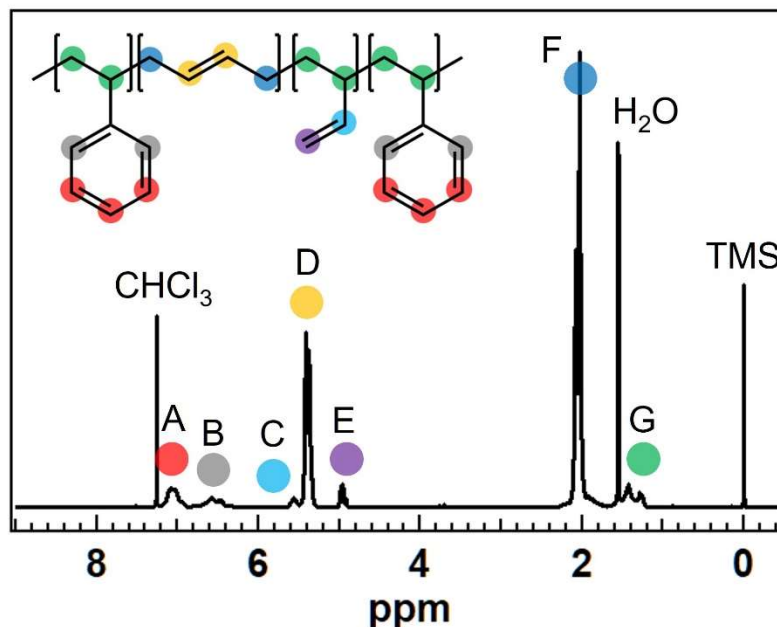


Figure S1. $^1\text{H-NMR}$ spectrum for SBS.

Table S1. Integral ratios of characteristic signals for SBS in Figure S1

Signal	Integral ratios
A	3.09
B	2.00
C	0.68
D	10.77
E	1.15
F	23.86
G	6.03

We here estimate the mass fraction of poly(styrene) blocks (ϕ_{PS}) in SBS as follows. The value of ϕ_{PS} can be estimated by,

$$\phi_{\text{PS}} = \frac{(I_B \times m_{\text{styrene}})/2}{\{(I_B \times m_{\text{styrene}}) + (I_D \times m_{1,4\text{-butadiene}}) + (I_E \times m_{1,2\text{-butadiene}})\}/2} \quad (\text{S1})$$

, where I is the integral ratio for each signal. In equation (S1), 2 in the numerator and denominator is needed since these integrals correspond to two protons each. m corresponds to the formula mass of each unit: 104.15 g/mol for styrene (m_{styrene}), 54.1 g/mol for butadiene 1,2- and 1,4-adducts ($m_{1,2\text{-butadiene}}$ and $m_{1,4\text{-butadiene}}$), respectively. The resulting ϕ_{PS} was ca. 0.24.

In Figure S2, the spectrum for SBS-OH is provided. New signals attributed to $-S-\underline{CH}_2-\underline{CH}_2-OH$ groups were observed at 2.7 ppm and 3.7 ppm, indicating the successful attachment of OH groups to the poly(butadiene) block. The integral ratios are summarized in Table S2.

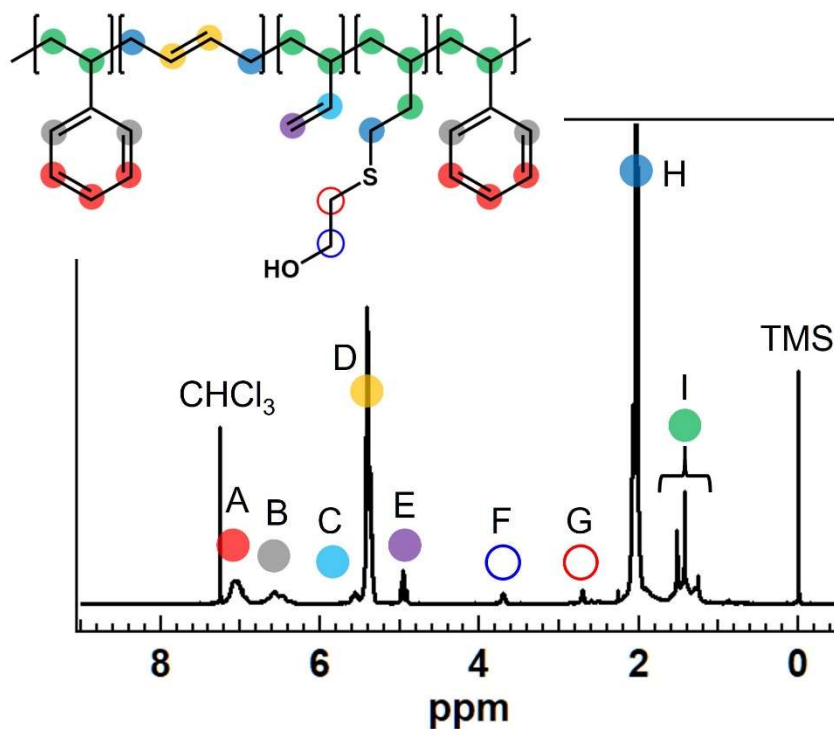


Figure S2. 1H -NMR spectrum for SBS-OH.

Table S2. Integral ratios of characteristic signals for SBS-OH in Figure S2

Signal	Integral ratios
A	3.14
B	2.00
C	0.48
D	10.23
E	0.85
F	0.57
G	0.72
H	23.13
I	6.58

In Figure S3, the spectrum for SBS-Py is provided. New signals from pyridine groups were observed at 7.8 ppm and 8.8 ppm, and signals from $-S-CH_2-CH_2-$ were shifted to 2.8 ppm and 4.5 ppm. These results indicate the attachment of pyridine groups through esterification reactions of the OH groups in SBS-OH. The integral ratios are summarized in Table S3.

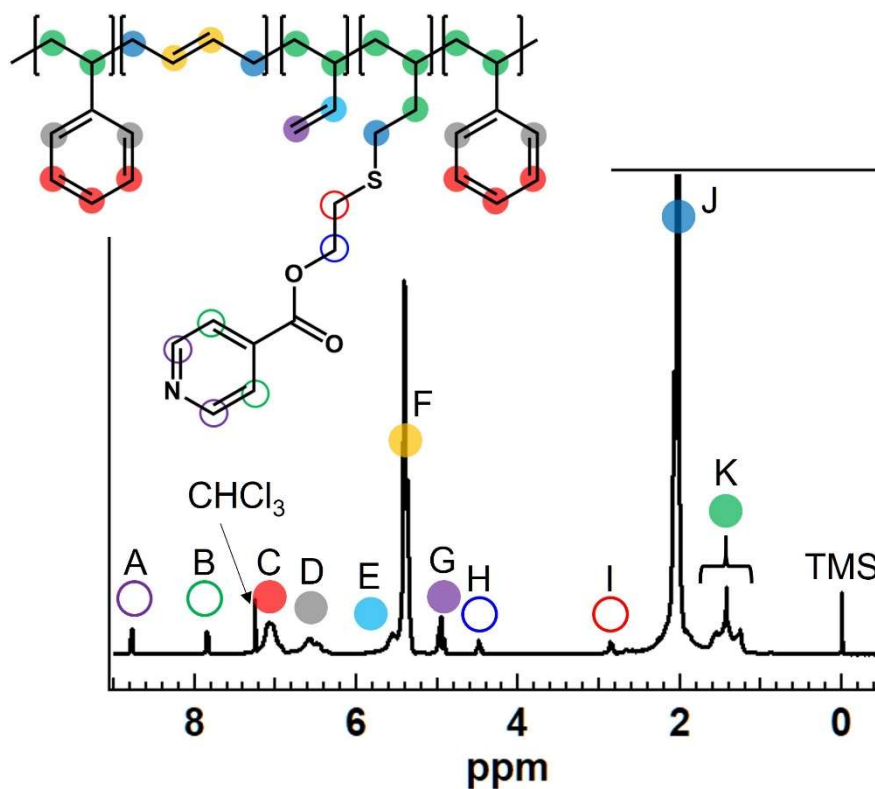


Figure S3. ^1H -NMR spectrum for SBS-Py.

Table S3. Integral ratios of characteristic signals for SBS-Py in Figure S3

Signal	Integral ratios
A	0.55
B	0.55
C	3.29
D	2.00
E	0.48
F	10.66
G	0.92
H	0.55
I	0.61
J	23.52
K	6.55

We here estimate the mass fraction of poly(styrene) blocks (ϕ_{PS}) in SBS-Py as follows. The value of ϕ_{PS} can be estimated by,

$$\phi_{PS} = \frac{(I_D \times m_{styrene})/2}{\{(I_A \times m_{Py-butadiene}) + (I_D \times m_{styrene}) + (I_F \times m_{1,4-butadiene}) + (I_G \times m_{1,2-butadiene})\}/2} \quad (S2)$$

, where I is the integral ratio for each signal. In equation (S2), 2 in the numerator and denominator is needed since these integrals correspond to two protons each. m corresponds to the formula mass of each unit: 104.15 g/mol for styrene ($m_{styrene}$), 54.1 g/mol for butadiene 1,2- and 1,4-adducts ($m_{1,2-butadiene}$ and $m_{1,4-butadiene}$) and 237.88 g/mol for pyridine-attached butadiene ($m_{Py-butadiene}$), respectively. The resulting ϕ_{PS} was ca. 0.22. This value is reasonable, considering the ϕ_{PS} estimated for original SBS ($\phi_{PS} \sim 0.24$).

The molecular weight between the pyridine groups (i.e., equivalent molecular weight of the pyridine group) in the middle block was estimated using signals of A, F, and G. The ratio of integrals for these signals provide the unit mole ratio of pyridine-attached poly(butadiene) units and original poly(butadiene) units as, pyridine-attached poly(butadiene) : poly(butadiene), 1,4-adduct : poly(butadiene), 1,2-adduct = 0.55 : 10.66 : 0.92 = 1 : 19.38 : 1.67. Since this ratio represents the equivalent repeating units per pyridine group, the equivalent molecular weight of the pyridine group can be estimated as $1 \times 237.1 + 19.38 \times 54.1 + 1.67 \times 54.1 \sim 1.4k$, using the formula mass of corresponding units.

2. SEC data

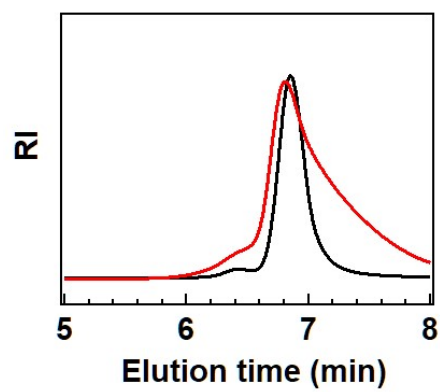


Figure S4. SEC data for (black) SBS and (red) SBS-Py.

3. FT-IR

First, Figure S5 represents the data obtained for poly(acrylate) bearing pyridine side groups (coded as Py-12) and the cross-linked sample (coded as CL-12) after reacting Py-12 with 1,6-diiodohexane. The data was reproduced from our previous study.^{S1} The signal from the free pyridine group is observed at ca. 1600 cm^{-1} , whereas the signal from quaternized pyridine is observed at ca. 1640 cm^{-1} .

Figure S6 provides the FT-IR spectrum for SBS. According to the literature, a signal at 1600 cm^{-1} from ring breathing of the benzene ring,^{S2} and a signal at 1640 cm^{-1} is derived from the C=C stretching vibrations of poly(butadiene).^{S3}

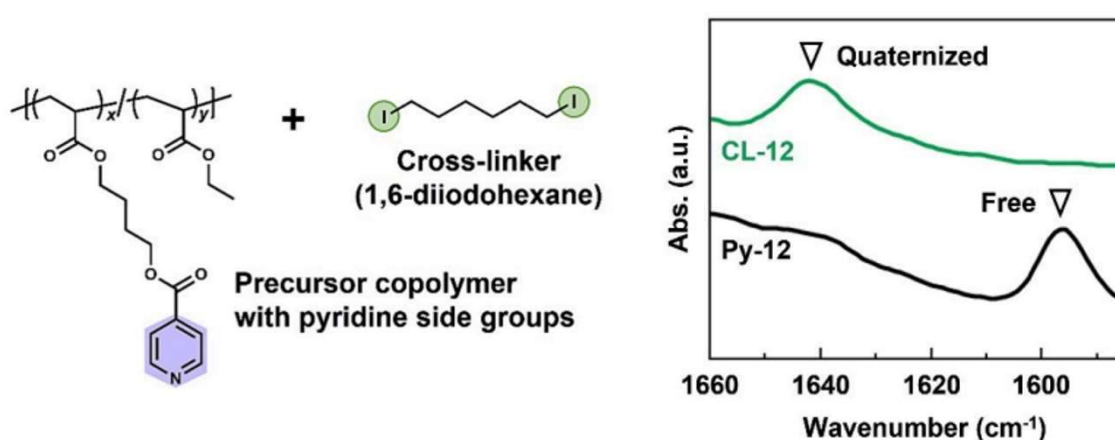


Figure S5. FT-IR data for poly(acrylate) bearing pyridine side groups (coded as Py-12) and the cross-linked samples (coded as CL-12) after reacting Py-12 with 1,6-diiodohexane. Adapted from *European Polymer Journal*, 208, M. Hayashi et al., Intrinsic differences of unentangled and highly entangled vitrimer-like materials with bond exchangeable nanodomains, 112862, Copyright (2024), with permission from Elsevier.

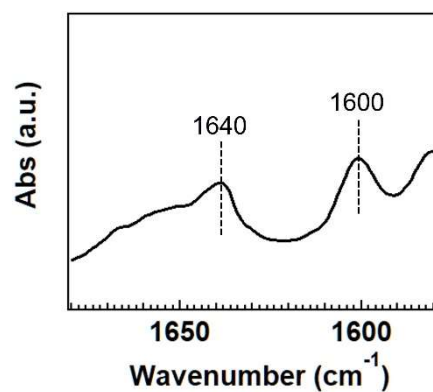


Figure S6. FT-IR spectrum for SBS.

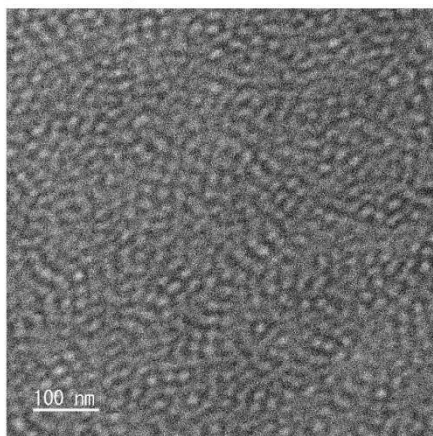
S1) T. Kito and M. Hayashi, *Eur. Polym. J.*, 2024, **208**, 112862.

S2) D. Olmos, E. V. Martín and J. González-Benito, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24339-24349.

S3) B. Orwat, R. Januszewski, M. Dutkiewicz and I. Kownacki, *Ind. Eng. Chem. Res.*, 2023, **62**, 10309-10319.

4. TEM observation

(a) SBS-Py



(b) SBS-CL-1

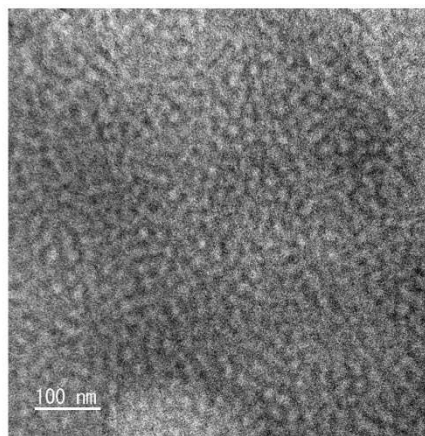


Figure S7. TEM images for (a) SBS-Py and (b) SBS-CL-1, where the darker region corresponds to the poly(butadiene) matrix.

5. Fitting analysis for the SAXS data of SBS-CL-1

A fitting analysis was conducted for the scattering from the subdomains in the data of SBS-CL-1, according to the Yarusso-Cooper (Y-C) model.^{S4} The entire function is described by,

$$I(q) = K \frac{V_1^2}{V_p} \Phi(qR_1)^2 \frac{1}{1 + (\frac{8V_{CA}}{V_p}) \Phi(2qR_{CA})} \quad (\text{S3})$$

$$V_{CA} = \frac{4}{3} \pi R_{CA}^3 \quad (\text{S4})$$

$$V_1 = \frac{4}{3} \pi R_1^3 \quad (\text{S5})$$

$$\Phi(x) = 3 \frac{\sin x - x \cos x}{x^3} \quad (\text{S6})$$

In the above function, the spherical-shaped aggregates with radius R_1 are assumed to be distributed randomly while maintaining the radius of closest approach R_{CA} , where R_{CA} governs the spatial correlation between neighboring aggregates. V_p represents the average sample volume per aggregate, and K determines the peak amplitude. The experimental spectrum was fitted by adjusting the parameters, R_1 , R_{CA} , V_p , and K (Figure S8). The obtained values are 2.11 nm for R_1 and 3.56 nm for R_{CA} , 430.27 nm³ for V_p , and 401.54 for K . From the values of R_1 and V_p , we estimated the distance (d_a) between the aggregates, according to,^{S5}

$$d_a = 2 \times \left\{ \left(\frac{1}{V_1} \cdot \frac{3}{4\pi} \right)^{1/3} - R_1 \right\} \quad (\text{S7})$$

The resulting value of d_a was ca. 5.16 nm.

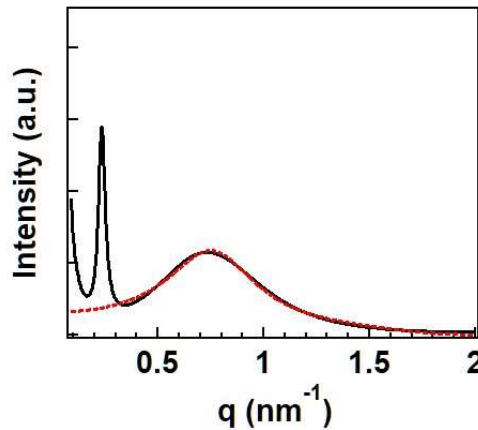


Figure S8. Fitting curve for SBS-CL-1 based on the Y-C model.

S4) D. J. Yarusso and S. L. Cooper, *Macromolecules*, 1983, **16**, 1871-1880.

S5) Y. Miwa , J. Kurachi , Y. Sugino , T. Udagawa and S. Kutsumizu, *Soft Matter*, 2020, **16** , 3384-3394.

6. Temperature-ramp SAXS data

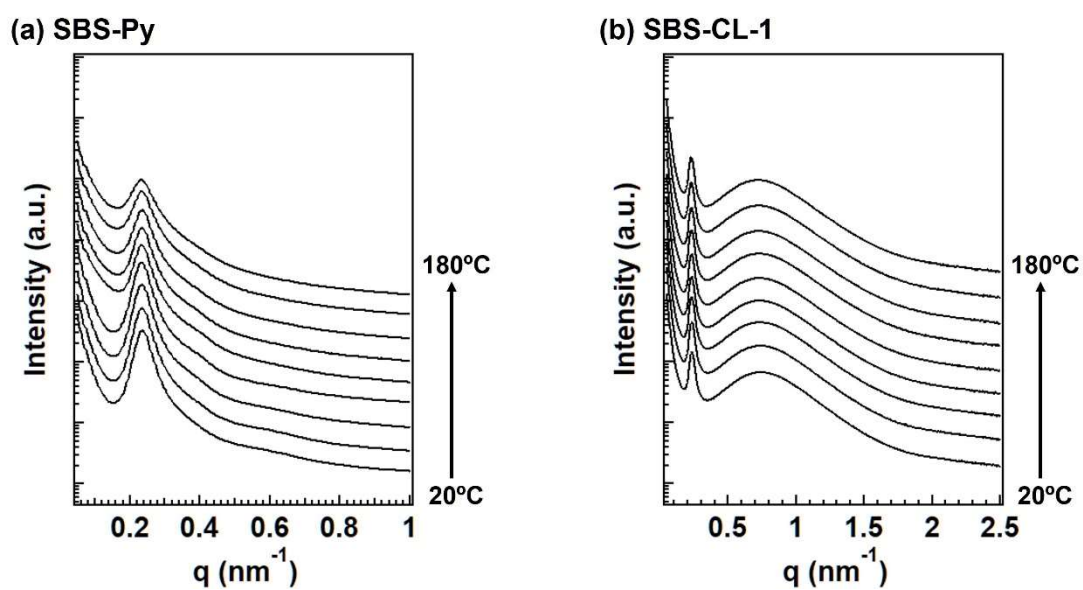


Figure S9. Temperature-ramp SAXS spectra for (a) SBS-Py and (b) SBS-CL-1, where the temperature range was from 20 °C to 180 °C with an interval of 20 °C.

7. TGA thermogram

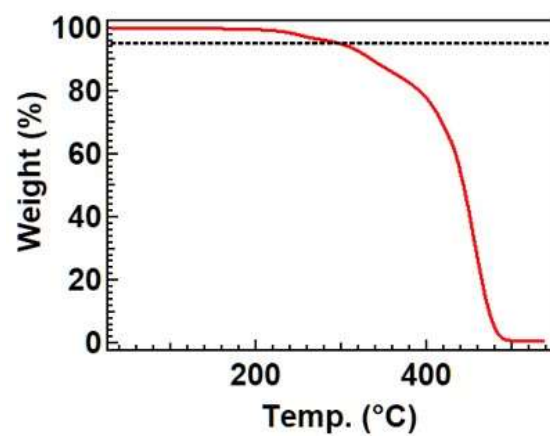


Figure S10. TGA thermogram for SBS-CL. The dotted line indicates the 5% weight loss.

8. Non-normalized stress relaxation curves

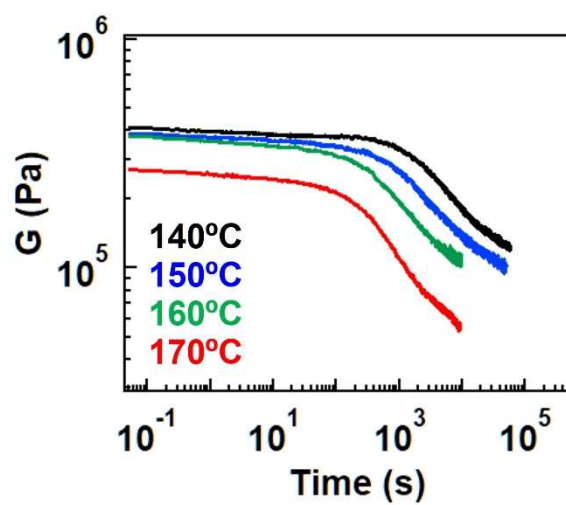


Figure S11. Non-normalized stress relaxation curves for SBS-CL-1.

9. Comparison of stress relaxation for three samples

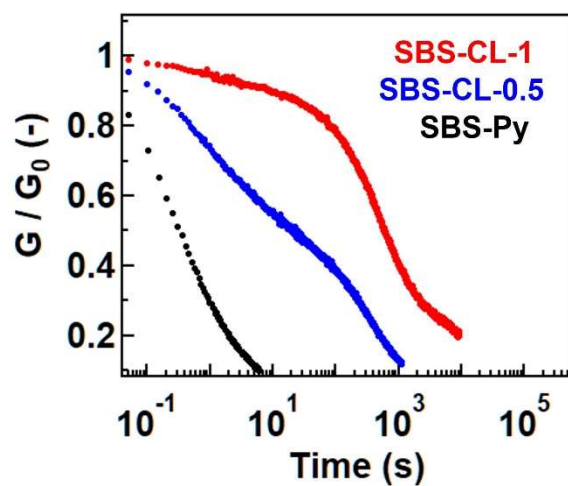


Figure S12. Comparison of stress relaxation behaviors for SBS-Py, SBS-CL-0.5, and SBS-CL-1, measured at 170 °C, where the Y-axis indicates the relaxation modulus (G) normalized by the initial modulus (G_0) at $t = 0$.

10. Arrhenius plots of relaxation time

Table S4. The summary of relaxation time (τ) for SBS-CL-1

Temperature	τ (s)
170 °C	1265
160 °C	2618
150 °C	7653
140 °C	16835

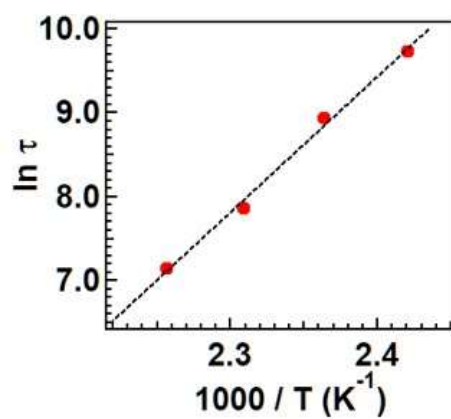


Figure S13. Plots of $\ln \tau$ as a function of inverse temperatures.