

## Supporting Information

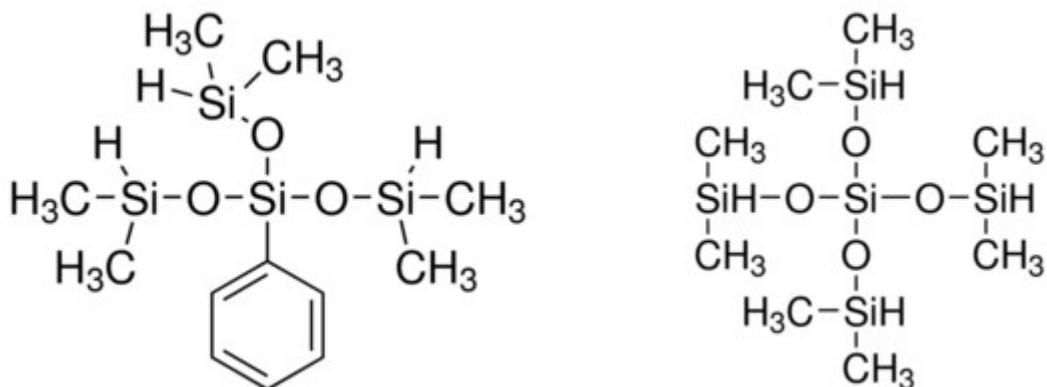
# A Multiple Length Scale Description of the Mechanism of Elastomer Stretching

Joerg Neuefeind<sup>1</sup>, Anne L. Skov<sup>2\*</sup>, John Daniels<sup>3,4</sup>, Veijo Honkimäki<sup>4</sup>, Bo Jakobsen<sup>5</sup>, Jette Oddershede<sup>6</sup>,  
Henning F. Poulsen<sup>6</sup>

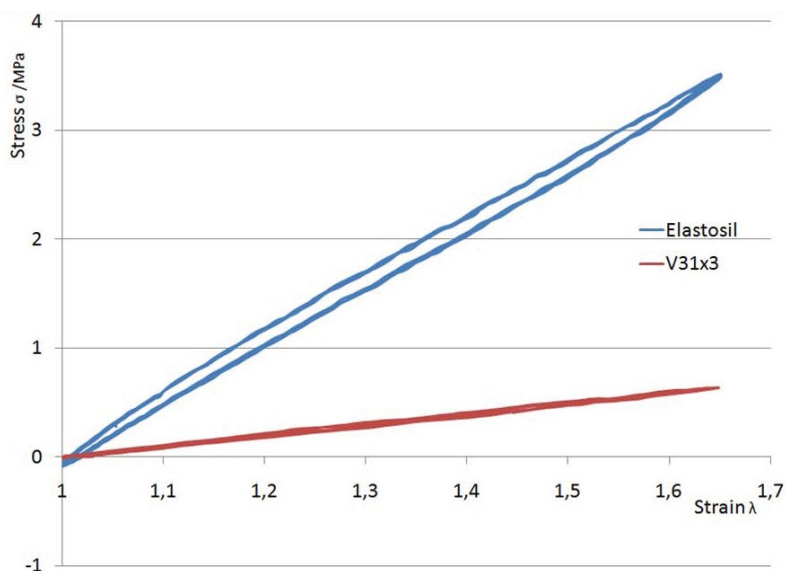
*1 Spallation Neutron Source, Oak Ridge National Laboratory, MS 6475, PO Box 2008, Oak Ridge, TN, 37831. 2 Danish Polymer Centre, DTU Chemical Engineering, Søltofts Plads, DK-2800 Kgs. Lyngby, Denmark. 3 School of Materials Science and Engineering, UNSW Australia, Kensington 2052, NSW, Australia. 4 European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France. 5 DNRF Centre "Glass and Time," IMFUFA, Department of Sciences, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark. 6 Neutrons and X-rays for Materials Physics, DTU Physics, Fysikvej, DK-2800 Kgs. Lyngby, Denmark.*

\*Corresponding author: A.L.Skov: [al@kt.dtu.dk](mailto:al@kt.dtu.dk)

## S1. Details of Characterization



**Figure S1.** The applied crosslinkers for the silylation based crosslinking reaction. Left: The three-functional crosslinker (Tris(dimethylsiloxy)phenylsilane). Right: The four-functional crosslinker (Tetrakis(dimethylsilyl) orthosilicate).



**Figure S2.** Mechanical properties. Reversing large amplitude oscillatory elongation on the strongest (Elastosil) and softest (V31) networks. The strain rate is  $\nu = 0.02 \text{ s}^{-1}$ .

Table S1: Properties of the applied polymers. The molecular weight  $M_n$  was determined by Size Exclusion Chromatography. The polydispersity index,  $PDI = M_w/M_n$ , was determined by  $^1H$  NMR measurements. The methods are described in (13).

Polymer	$M_n$ [g/mol]	PDI
V31	29,000	1.3
V35	49,500	1.5
V41	62,400	1.6

Table S2: Average bond lengths ( $r$ ) and associated widths ( $\sigma$ ) in the distance distributions as well as derived average bond angles for sample V31 in the loaded and un-loaded state. The parameters result from a fit of the isotropic experimental data in Fig 2a to the scattering arising from a model of the structural unit. <sup>1</sup>: Fit of  $\sigma$  is restricted to values larger than 0.08 Å,  $|\Delta\sigma|$  to values greater than 10% of  $\sigma$ .

	$r_0, \sigma$ ( $\lambda=1$ )	$\Delta r, \Delta\sigma$ ( $\lambda=2 - \lambda=1$ )	Relative change $\Delta r/r_0, \Delta\sigma/\sigma$
$r_{SiO} / \text{Å}$	1.642	$-6.0 \cdot 10^{-4}$	$-3.7 \cdot 10^{-4}$
$\sigma_{SiO} / \text{Å}$	0.111	$4.5 \cdot 10^{-3}$	$4.0 \cdot 10^{-2}$
$r_{SiC} / \text{Å}$	1.869	$-2.8 \cdot 10^{-4}$	$-1.5 \cdot 10^{-4}$
$\sigma_{SiC} / \text{Å}$	0.143	$4.4 \cdot 10^{-3}$	$3.1 \cdot 10^{-2}$
$r_{SiSi} / \text{Å}$	3.160	$-4.2 \cdot 10^{-4}$	$-1.3 \cdot 10^{-4}$
$\sigma_{SiSi} / \text{Å}$	0.139	$3.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-2}$
$r_{OO} / \text{Å}$	2.736	$1.2 \cdot 10^{-3}$	$4.6 \cdot 10^{-4}$
$\sigma_{OO} / \text{Å}$	<sup>1</sup> 0.080	$-5.4 \cdot 10^{-3}$	$-6.8 \cdot 10^{-2}$
$r_{CC} / \text{Å}$	3.055	$-10.4 \cdot 10^{-3}$	$-3.4 \cdot 10^{-3}$
$\sigma_{CC} / \text{Å}$	<sup>1</sup> 0.080	$7.8 \cdot 10^{-3}$	$9.7 \cdot 10^{-2}$
$r_{OC} / \text{Å}$	2.858	$1.0 \cdot 10^{-4}$	$3.6 \cdot 10^{-5}$
$\sigma_{OC} / \text{Å}$	0.200	$1.2 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$
$\langle OSiO \rangle / \text{deg}$	112.8	$7.9 \cdot 10^{-2}$	$7.0 \cdot 10^{-4}$
$\langle CSiC \rangle / \text{deg}$	109.6	$-5.5 \cdot 10^{-1}$	$-5.0 \cdot 10^{-3}$
$\langle SiOSi \rangle / \text{deg}$	148.4	$-5.3 \cdot 10^{-2}$	$-3.6 \cdot 10^{-4}$

**Table S3:** The results for the preferred orientation parameter is obtained by scaling the model described in the main text to the amplitude of  $g_2$  in Fig S4b, and reflects the increased likelihood of a SiO bond to point in the tensile direction compared to an isotropic distribution at  $\lambda=2$ . <sup>1</sup>The values for V41 and Elastosil are extrapolated to  $\lambda=2$ .

Polymer	V31	V35	V41	Elastosil
Preferred orientation parameter / %	1.9	0.2	0.6 <sup>1</sup>	1.4 <sup>1</sup>

## S2. Details of Entropic and Enthalpic Contributions

The entropy of stretching of polymer chains is generally written in the simplified form under the assumption that the polymer chains behave according to Gaussian random walks<sup>1</sup>:

$$\Delta S = -\frac{3}{2}k \frac{R^2}{R_o^2} = -\frac{3}{2}k \frac{R^2}{Nb^2} \quad (\text{S1})$$

Where  $k$  is the Boltzmann's constant,  $R$  and  $R_o$  are the perturbed and unperturbed end-to-end distances of the polymer, respectively, and  $N$  is the number of Kuhn steps of length  $b$ .

If the chains are confined by entanglements moving affinely with the deformation, the change in entropy upon stretching of a polymer chain with  $N/N_e$  entangled chains can be expressed as:

$$\Delta S' = -\frac{3}{2}k \frac{N}{N_e} \frac{R_n^2}{N_e b^2} \quad (\text{S2})$$

Where  $N_e$  is the number of Kuhn steps in an entanglement and  $R_n$  is the perturbed end-to-end length of the chain segment with the characteristic entanglement length.

If we assume simplistically that we allow one entanglement to slide upon the deformation, the two surrounding polymer segments, each of length  $N_e b$ , are replaced with two polymer segments of approximate lengths 0 and  $2N_e b$ . The entropy of stretching of such a configuration can be written:

$$\Delta S'' = -\frac{3}{2}k \left( \left( \frac{N}{N_e} - 2 \right) \frac{R_n^2}{N_e b^2} + \frac{2R_n^2}{2N_e b^2} \right) = -\frac{3}{2}k \left( \frac{N}{N_e} - 1 \right) \frac{R_n^2}{N_e b^2} \quad (\text{S3})$$

Since entropy is a state function, the gained entropy from entanglement sliding in the stretched state can be calculated as:

$$\Delta S_{slide} = \Delta S'' - \Delta S' = \frac{3}{2}k \frac{R_n^2}{N_e b^2} \quad (S4)$$

In other words, when the entanglement is sliding, the decrease in entropy upon stretch is minimized and thus entropy is maximized and this can be facilitated by stretching the chains.

The magnitude of enthalpy is evaluated by the expression from Khazanovich<sup>2</sup>:

$$\frac{F_e}{F} = - \frac{\varepsilon \partial g}{f \partial \varepsilon} / \frac{\partial f}{\partial g} \quad (S5)$$

Where  $F$  is the total stretching force,  $F_e$  is the enthalpic contribution to the stretching force,  $\varepsilon$  is the reduced stiffness,  $f$  is dimensionless force, and  $g$  is the degree of chain stretching given by:

$$\varepsilon = \frac{b^2 K_s}{kT} \quad (S6)$$

$$f = \frac{bF}{kT} \quad (S7)$$

$$g = \frac{\langle h_f \rangle}{Nb} \quad (S8)$$

Where  $K_s$  is the stiffness coefficient of the Kuhn segment and  $h_f$  is the projection of the vector connecting the ends of the chains onto the stretching axis.

The solution to the above equation in terms of the degree of chain stretching can be written under the assumption that  $\varepsilon \gg 1$ :

$$g = \frac{f}{\varepsilon} - \frac{1}{f} + \frac{(\varepsilon + 1) + \coth(f)}{\varepsilon + f \coth(f)} \quad (S9)$$

The assumption is not strictly correct as the Si-O bonds are rather flexible but the assumption does not change the order of magnitude of the solution.

If we assume that the allowed stretching force is of the order of several  $kT$  according to the results for the entropy gain from sliding, the  $\coth(f)$  reduces to 1 and the expression can be simplified to:

$$g = \frac{f}{\varepsilon} - \frac{1}{f} + \frac{(\varepsilon + 1) + f}{\varepsilon + f} = 1 + \frac{f}{\varepsilon} - \frac{1}{f} + \frac{1}{\varepsilon + f} \quad (S10)$$

Further assuming that the reduced stretching force is greater than the reduced stiffness, i.e.  $f \gg \varepsilon$ , following simplified equation is obtained:

$$g = 1 + \frac{f}{\varepsilon} = 1 + \frac{\frac{bF}{kT}}{b^2 K_s} = 1 + \frac{F}{bK_s} \sim 1 + \frac{T\Delta S_{slide}/b}{bK_s} \sim 1 + \frac{T\Delta S_{slide}}{b^2 K_s} \quad (S11)$$

Hereby it is shown by a very simplistic approach that the degree of chain stretching grows linearly with the entropy gain from allowing sliding of entanglements.

## List of references:

- S1. Flory, P.J., *Principles of Polymer Chemistry*, Ithaca: Cornell Univ. Press, 1953.
- S2. Khazanovich, T.N., *Doklady Physical Chemistry* **2009**, 425, 66–68.