Electronic Supplementary Information for:

Tailoring Single Chain Polymer Nanoparticle Thermo-Mechanical Behavior by Cross-link Density

Suwon Bae,[a] Or Galant,[b‡] Charles Diesendruck,[b‡] and Meredith Silberstein[a*]

[a] *Sibley School of Mechanical and Aerospace Engineering, Cornell University, NY14850 United States.*
[b] *Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel.*

Contents

Table S1 : Radius and radius of gyration of SCPNs as a function of degree of polymerization (DP) and degree of cross-linking (DC) at 300 K.

Table S2 : Radius and radius of gyration of 1000 monomer long linear collapsed chain and 10% cross-link SCPNs at 500 K, 300 K and 150 K.

Figure S1 : Distributions of 1000 monomer linear collapsed chain at 300K (a) Bond length (b) Bending angle (c) Dihedral torsional angle.

Figure S2 : Distributions of 1000 monomer 10% SCPN at 300K (a) Bond length (b) Bending angle (c) Dihedral torsional angle.

Figure S3 : Molecular structures of 1000 monomer long linear collapsed chain at 500 K, 300 K and 150 K.

Figure S4 : Cooling rate dependence of glass transition temperature, T_g.

Figure S5 : Alternative methods to determine the glass transition temperature of 1000 monomer long linear collapsed chain.

Figure S6 : Alternative methods to determine the glass transition temperature of 1000 monomer long 10% cross-link SCPN.

Figure S7 : Radial density distribution of equilibrated at 150 K (a) collapsed linear chains as a function of number of monomers, (b) 1000 monomer long chain and SCPNs as a function of degree of cross-linking.

Figure S8 : Snapshots of a MD simulation of 1000 monomer 10% cross-link SCPN under compression at 300 K. Red beads are standard monomers and blue beads are cross-linked monomers.

Figure S9 : Compression response of 500 monomer SCPN at 300 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

Figure S10 : Compression response of 500 monomer SCPN at 150 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

Figure S11 : Compression response of 2000 monomer SCPN at 300 K. (a) Stress versus sstrain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

Figure S12 : Compression response of 2000 monomer SCPN at 150 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

Figure S14 : Potential energy components of 1000 monomer SCPN during compression at 150 K. (a) Collapsed linear chain. (b) 5% cross-link SCPN. (c) 10% cross-link SCPN. (d) 15% cross-link SCPN.

Figure S15 : Energy per element of 1000 monomer 10% cross-link SCPN during compression at 300 K.

Figure S16 : Energy per element of 1000 monomer 10% cross-link SCPN during compression at 150 K.

Table S1: Radius and radius of gyration of linear collapsed chain and SCPNs as a function of degree of polymerization (DP) and degree of cross-linking (DC) at 300 K.

T	DP	DC	r (Å)	Spatial Deviation (%)	r_g (Å)
300 K	500	linear	18.424 ± 0.461	6.06	14.558 ± 0.089
		5% (s1)	18.424 ± 0.426	5.16	14.389 ± 0.074
		5% (s2)	18.061 ± 0.368	4.70	14.385 ± 0.077
		5% (s3)	18.135 ± 0.415	6.37	14.378 ± 0.104
		10% (s1)	17.865 ± 0.331	5.01	14.139 ± 0.063
		10% (s2)	18.285 ± 0.370	4.05	14.253 ± 0.059
		10% (s3)	17.896 ± 0.403	3.57	14.189 ± 0.036
		15% (s1)	18.477 ± 0.242	9.65	14.326 ± 0.096
		15% (s2)	18.300 ± 0.339	4.74	14.182 ± 0.055
		15% (s3)	18.732 ± 0.314	5.52	14.299 ± 0.062
	1000	linear	23.304 ± 0.409	3.34	18.262 ± 0.081
		5% (s1)	23.729 ± 0.516	2.84	18.297 ± 0.114
		5% (s2)	23.100 ± 0.363	5.69	18.196 ± 0.083
		5% (s3)	23.894 ± 0.432	6.71	18.143 ± 0.063
		10% (s1)	22.924 ± 0.301	7.47	18.112 ± 0.052
		10% (s2)	23.322 ± 0.384	7.30	17.942 ± 0.047
		10% (s3)	23.030 ± 0.309	5.42	17.907 ± 0.048
		15% (s1)	23.520 ± 0.283	11.17	18.164 ± 0.056
		15% (s2)	23.546 ± 0.241	3.38	17.934 ± 0.059
		15% (s3)	23.602 ± 0.375	7.06	17.974 ± 0.051
	2000	linear	29.665 ± 0.449	4.51	22.893 ± 0.052
		5% (s1)	29.215 ± 0.396	2.47	22.633 ± 0.048
		5% (s2)	30.447 ± 0.408	2.72	22.784 ± 0.058
		5% (s3)	29.345 ± 0.348	2.12	22.720 ± 0.048
		10% (s1)	30.472 ± 0.326	4.91	22.578 ± 0.042
		10% (s2)	28.902 ± 0.347	4.42	22.659 ± 0.044
		10% (s3)	29.537 ± 0.310	4.62	22.652 ± 0.054
		15% (s1)	29.448 ± 0.264	5.31	22.455 ± 0.036
		15% (s2)	29.211 ± 0.283	6.03	22.544 ±0.046
		15% (s3)	30.126 ± 0.255	2.38	22.670 ± 0.040

Table S2: Radius and radius of gyration of 1000 monomer long linear collapsed chain and 10% cross-link SCPNs at 500 K, 300 K and 150 K.

T	DP	DC	r (Å)	Spatial Deviation (%)	r_g (Å)
500 K	1000	linear	25.812 ± 0.782	6.03	19.489 ± 0.195
		10% (s1)	23.201 ± 0.106	4.31	18.009 ± 0.015
		10% (s2)	24.575 ± 0.066	1.44	17.864 ± 0.013
		10% (s3)	23.425 ± 0.089	6.99	18.042 ± 0.014
300 K	1000	linear	23.304 ± 0.409	3.34	18.262 ± 0.081
		10% (s1)	22.924 ± 0.301	7.47	18.112 ± 0.052
		10% (s2)	23.322 ± 0.384	7.30	17.942 ± 0.046
		10% (s3)	23.030 ± 0.309	5.42	17.907 ± 0.048
150 K	1000	linear	22.464 ± 0.134	5.86	17.919 ± 0.081
		10% (s1)	23.090 ± 0.137	8.27	18.031 ± 0.024
		10% (s2)	22.741 ± 0.132	8.57	17.865 ± 0.027
		10% (s3)	22.308 ± 0.117	3.98	17.668 ± 0.022

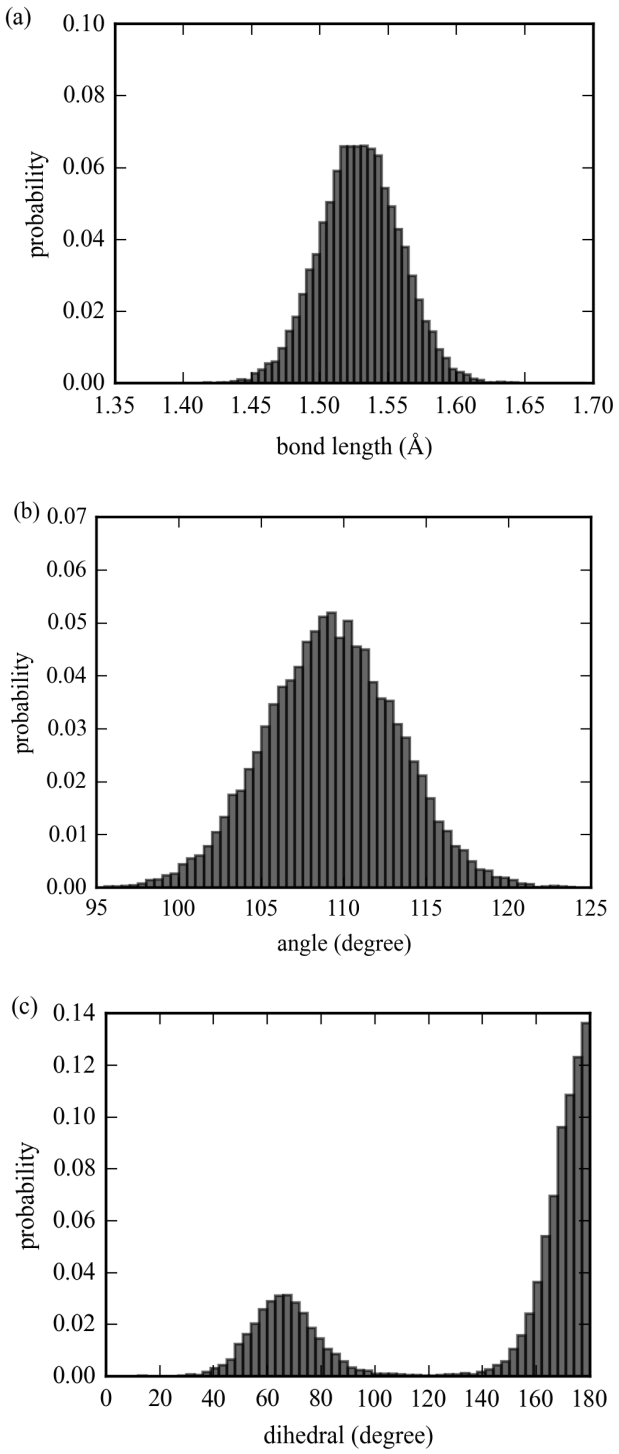

Figure S1: Distributions of 1000 monomer linear collapsed chain at 300K (a) Bond length (b) Bending angle (c) Dihedral torsional angle.

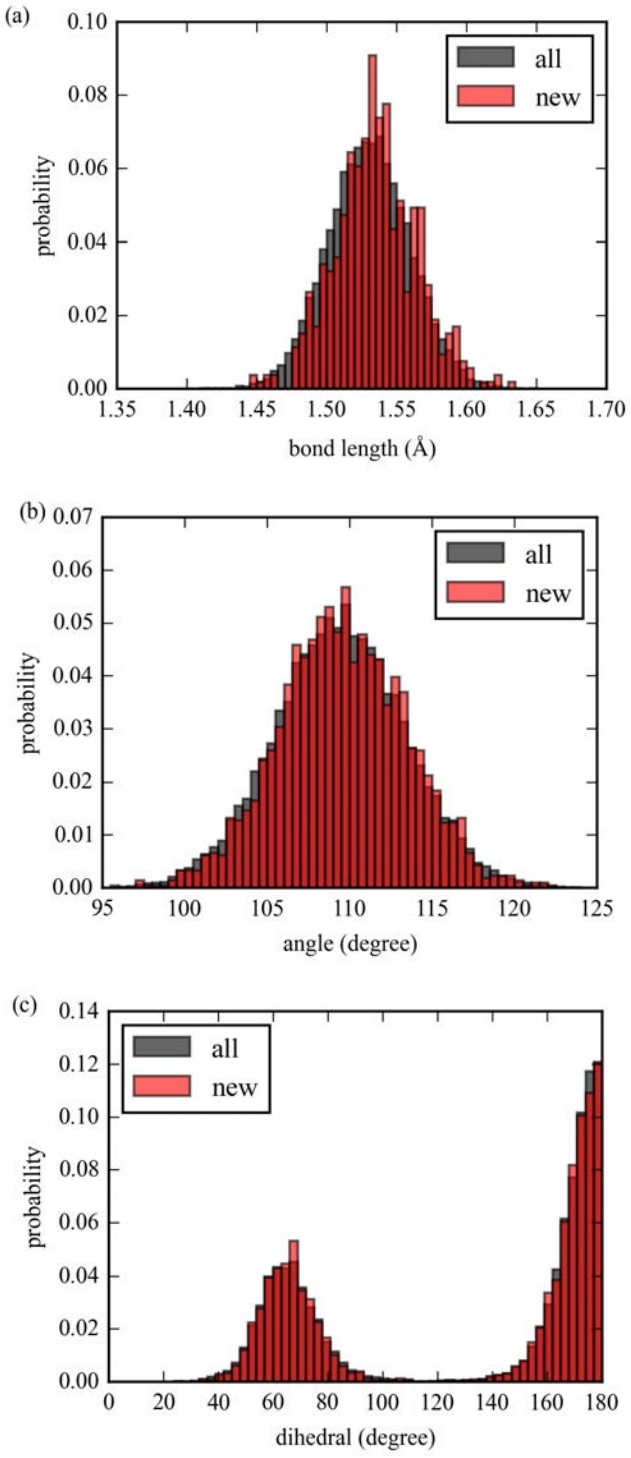

Figure S2: Distributions of 1000 monomer 10% SCPN at 300K (a) Bond length (b) Bending angle (c) Dihedral torsional angle.

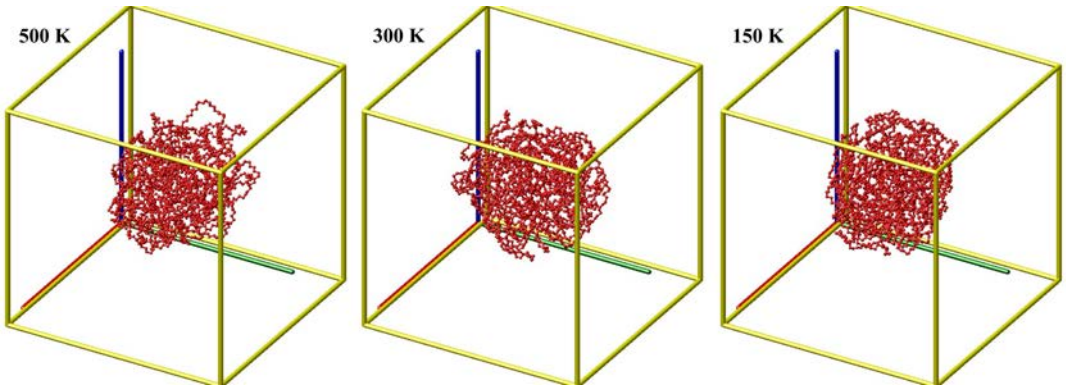

Figure S3: Molecular structures of 1000 monomer long linear collapsed chain at 500 K, 300 K and 150 K.

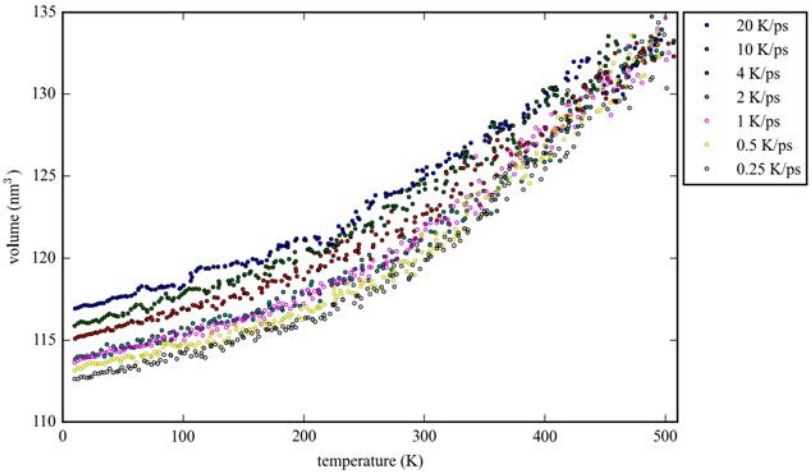

Figure S4: Cooling rate dependence of glass transition temperature, T_g.

Glass Transition Temperature

1) Temperature - Volume

The glass transition (T_g) temperature was determined by cooling the particles at a constant rate from 500 K down to 10 K while monitoring the volume. Molecular structures were extracted at discrete temperatures with an interval of about 5 K and loaded into Materials Studio to calculate the volume at each temperature. A curve was fitted to 100 pairs of volume versus temperature. Tangential lines were drawn at both ends of the fitted curve and the intersection of these two lines was taken as the T_g of that particle. This typical response is shown for the specific case of the 1000 monomer long linear collapsed chain (Figure S5 Top) and 10% cross-link SCPN (Figure S6 Top).

2) Temperature - Total energy

Described in the manuscript.

3) Self-intermediate scattering function

We determined T_g by means of the self intermediate scattering function, $F_s(k,t)$, the Fourier transform of the self van Hove function. It is expected that, as long as the motion of the polymer atoms is diffusional, at larger times $F_s(k,t)$ decays further than the function does at short times, implying that the decay would disappear when the glass transition takes place, resulting in a plateau in $F_s(k,t)$ at larger times.[1] The self intermediate scattering function, $F_s(k,t)$, was calculated at different temperatures between 150 K and 300 K. We observed the glass transition around 250K for both 1000 monomer long linear collapsed chain (Figure S5 Bottom) and 10% cross-link SCPN (Figure S6 Bottom).

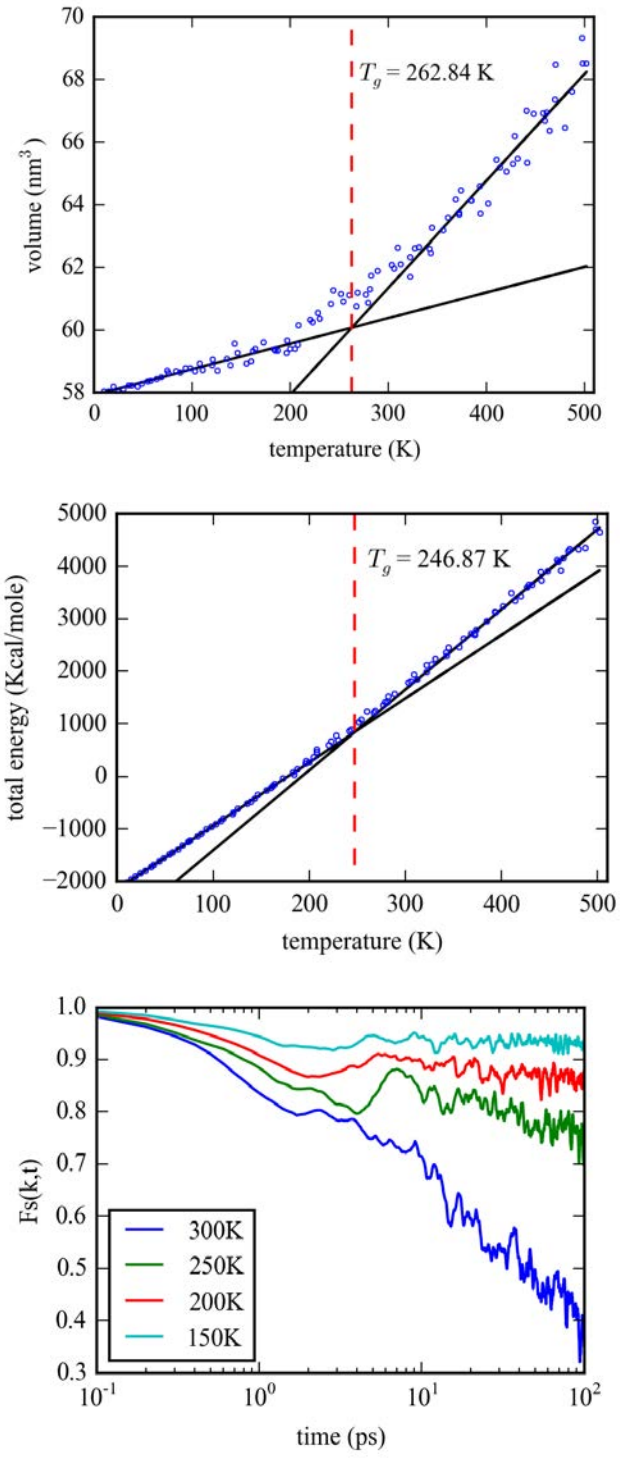

Figure S5: Alternative methods to determine the glass transition temperature of 1000 monomer long linear collapsed chain. (Top) Temperature - Volume (Middle). Temperature - Total energy. (Bottom) Time - Self-intermediate scattering function.

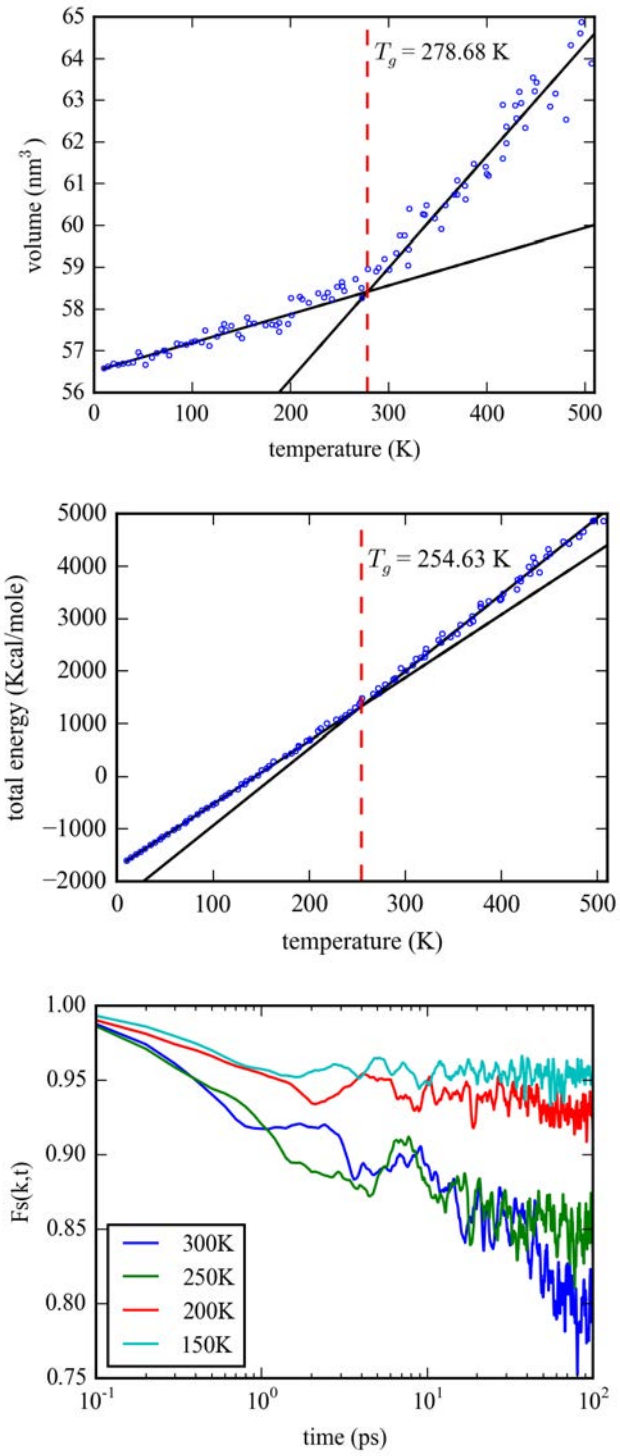

Figure S6: Alternative methods to determine the glass transition temperature of 1000 monomer long 10% cross-link SCPN. (Top) Temperature - Volume. (Middle) Temperature - Total energy. (Bottom) Time - Self-intermediate scattering function.

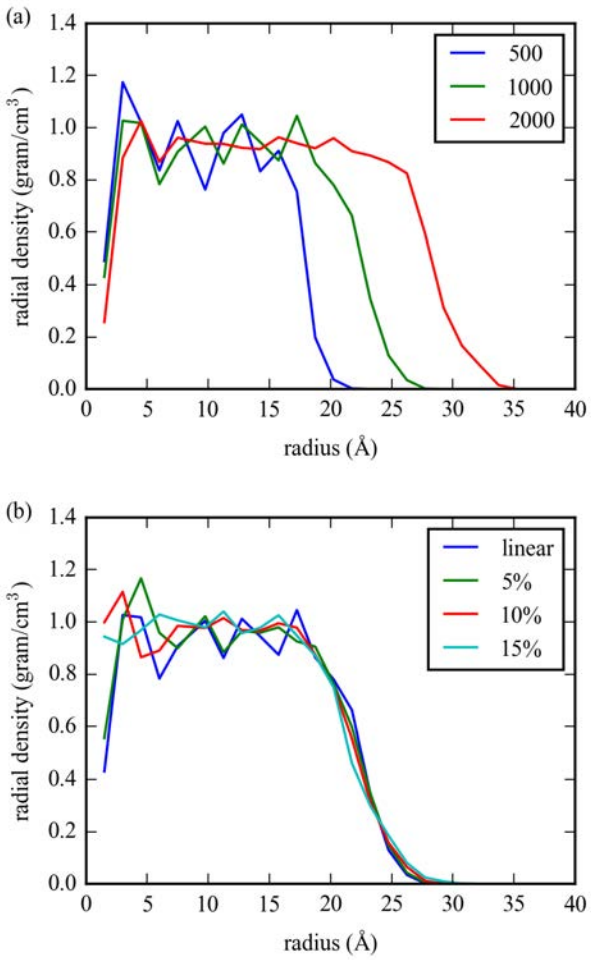

Figure S7: Radial density distribution of equilibrated at 150 K (a) collapsed linear chains as a function of number of monomers, (b) 1000 monomer long chain and SCPNs as a function of degree of cross-linking.

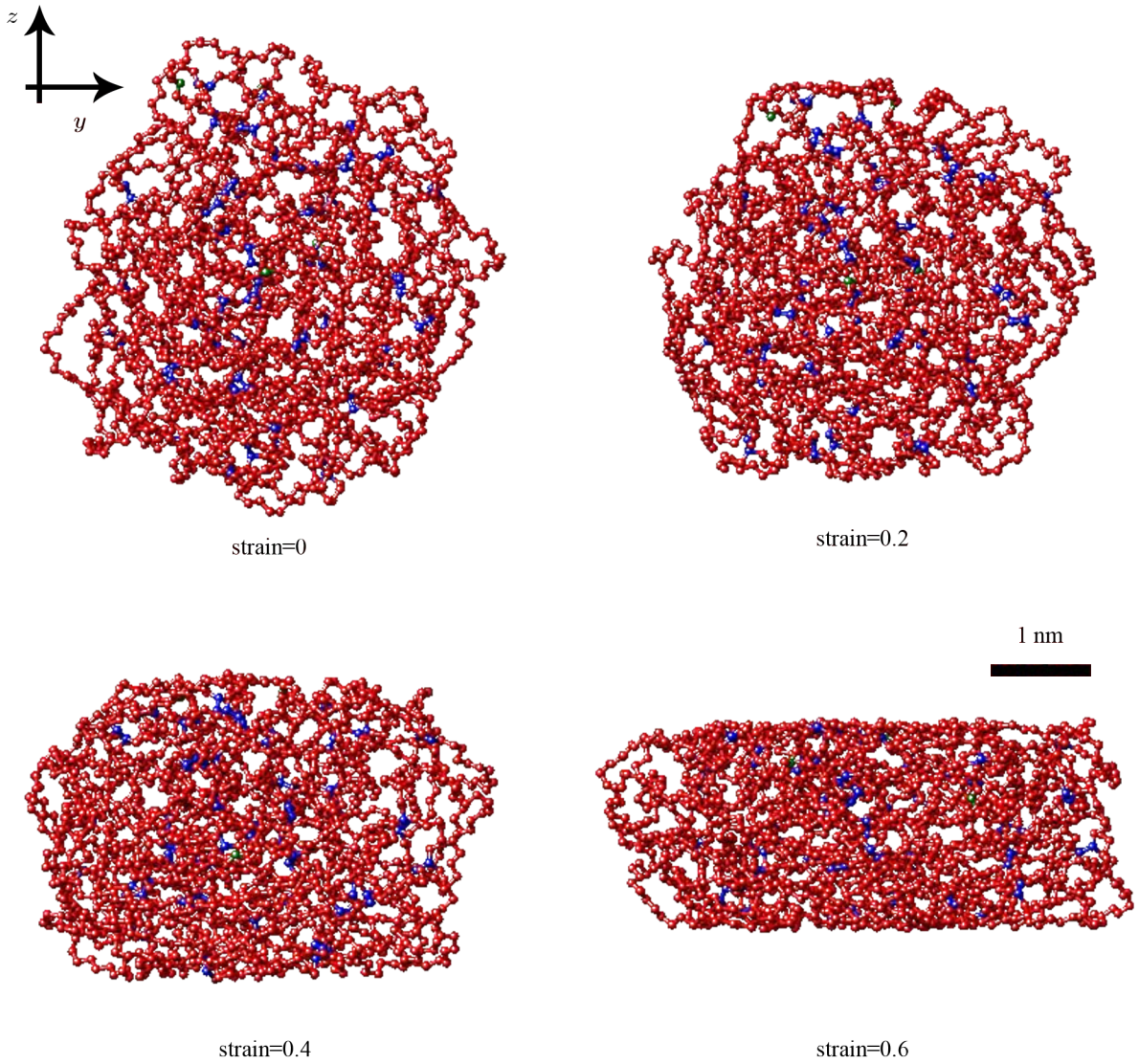

Figure S8: Snapshots of a MD simulation of 1000 monomer 10% cross-link SCPN under compression at 300 K. Red beads are standard monomers and blue beads are cross-linked monomers.

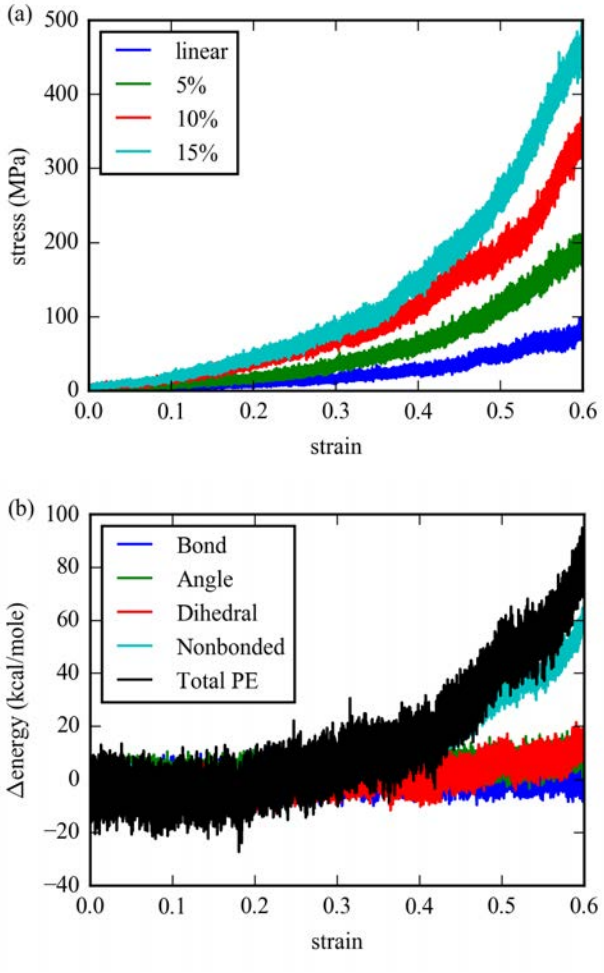

Figure S9: Compression response of 500 monomer SCPN at 300 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

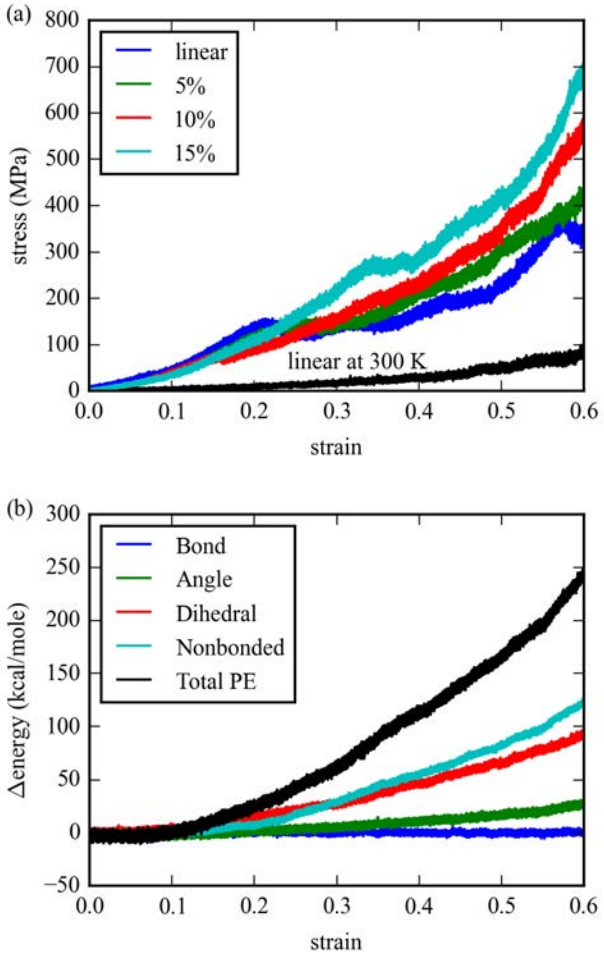

Figure S10: Compression response of 500 monomer SCPN at 150 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

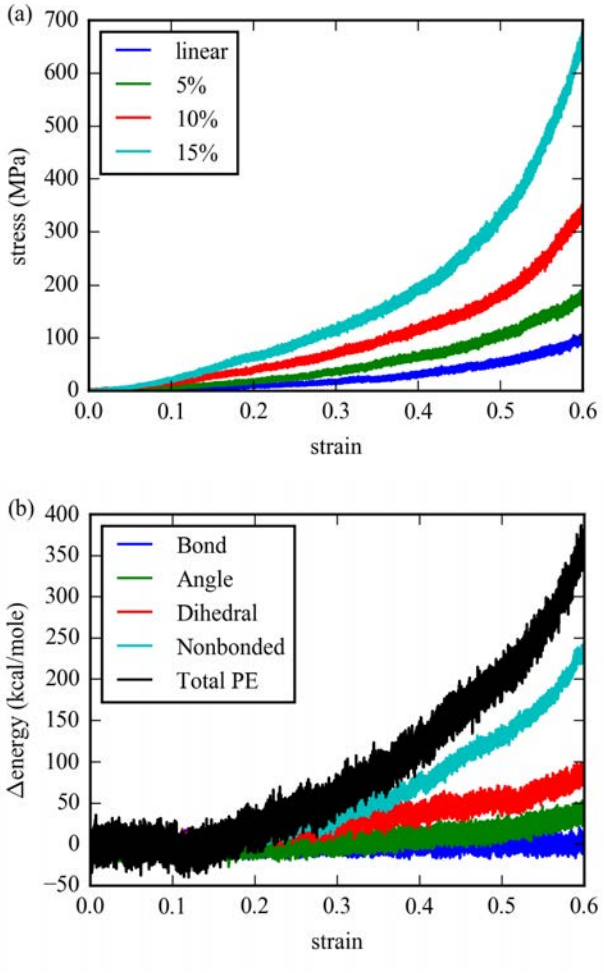

Figure S11: Compression response of 2000 monomer SCPN at 300 K. (a) Stress versus sstrain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

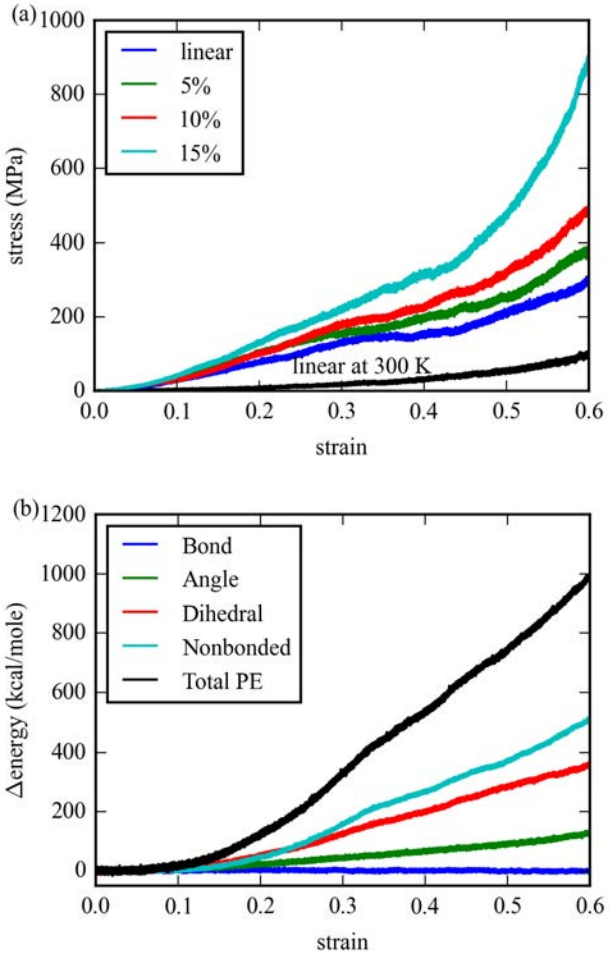

Figure S12: Compression response of 2000 monomer SCPN at 150 K. (a) Stress versus strain as a function of degree of cross-linking. (b) Potential energy components of 10% cross-link SCPN.

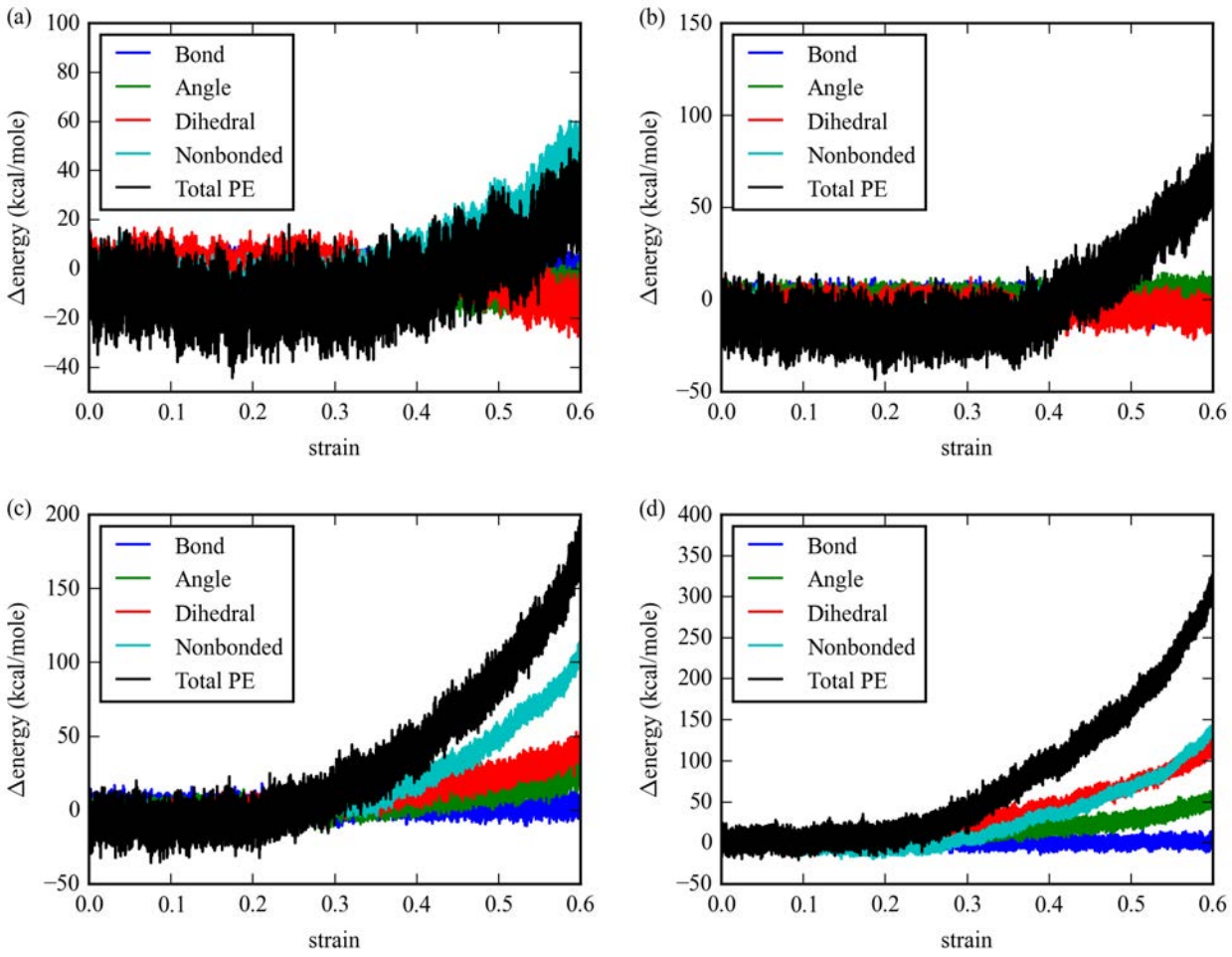

Figure S13: Potential energy components of 1000 monomer SCPN during compression at 300 K. (a) Collapsed linear chain. (b) 5% cross-link SCPN. (c) 10% cross-link SCPN. (d) 15% cross-link SCPN.

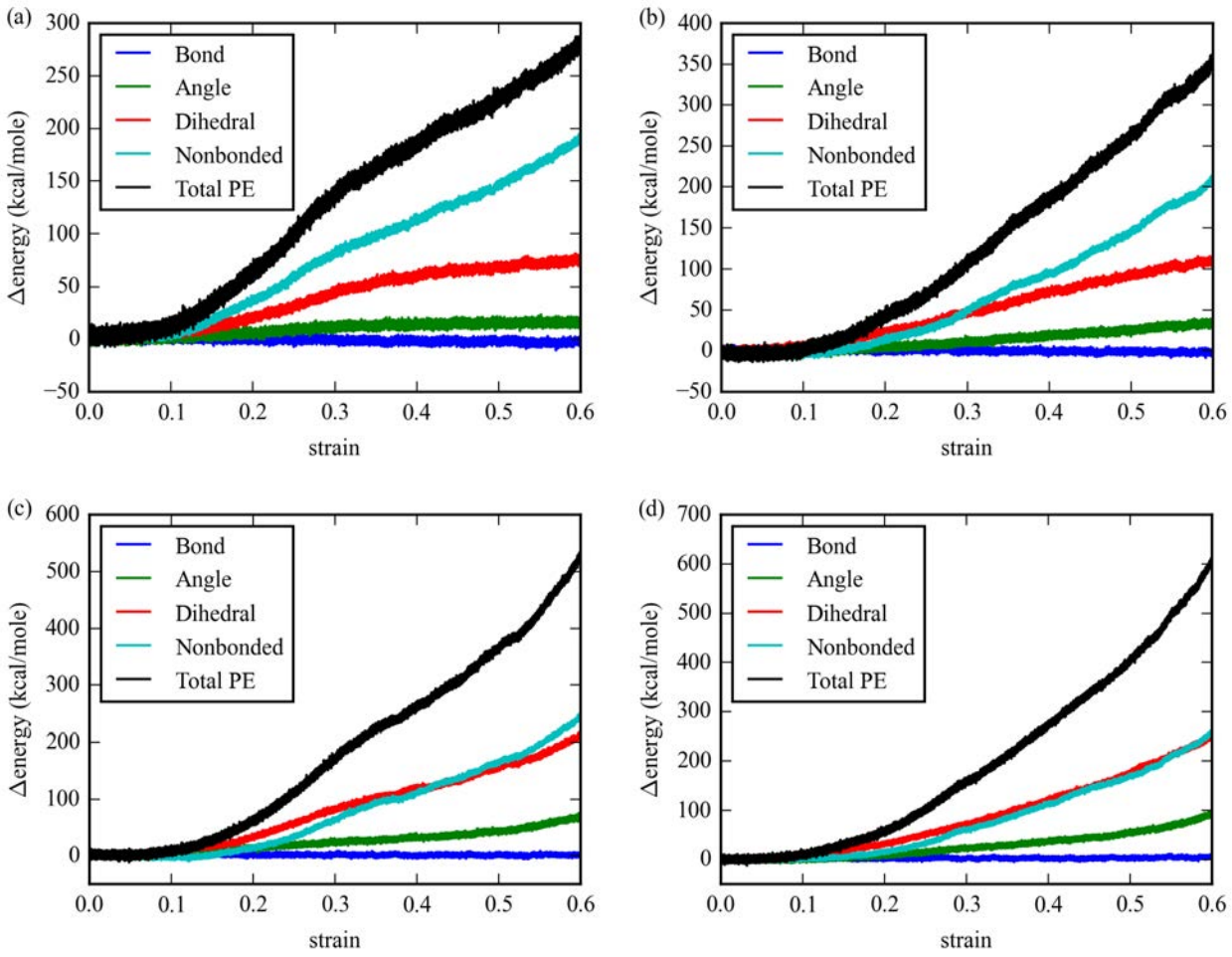

Figure S14: Potential energy components of 1000 monomer SCPN during compression at 150 K. (a) Collapsed linear chain. (b) 5% cross-link SCPN. (c) 10% cross-link SCPN. (d) 15% cross-link SCPN.

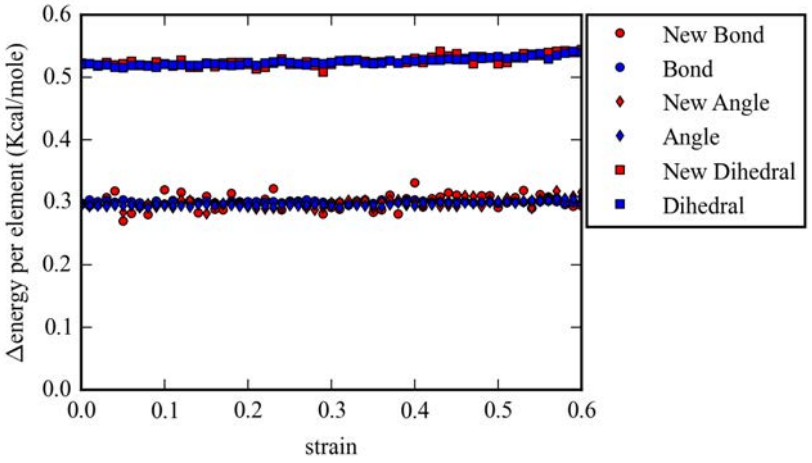

Figure S15: Energy per element of 1000 monomer 10% cross-link SCPN during compression at 300 K.

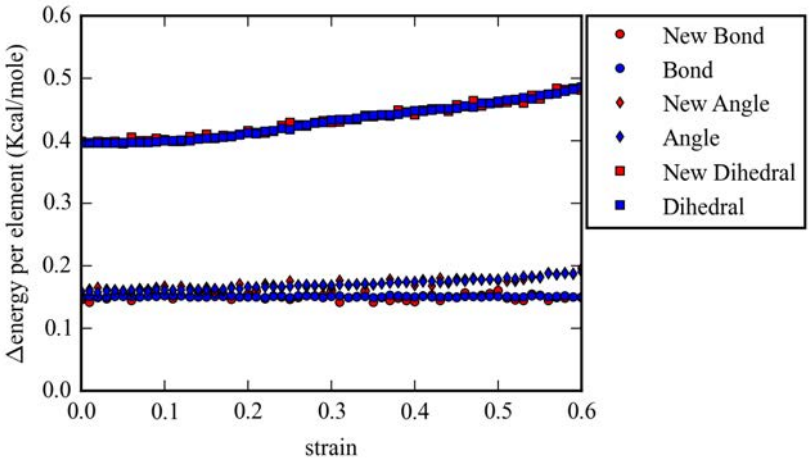

Figure S16: Energy per element of 1000 monomer 10% cross-link SCPN during compression at 150 K.

References

[1] N. F. a. van der Vegt, W. J. Briels, M. Wessling, and H. Strathmann. The sorption induced glass transition in amorphous glassy polymers. *The Journal of Chemical Physics*, 110(22):11061, 1999.