A Molecular Model For HNBR With Tunable Cross-Link Density

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S1: Force-field parameters and force-field analytical formulation
S2: Volume-temperature plot for T_g

S1: Force-field

CT = sp^3 carbon, CM = sp^2 carbon, CZ = sp carbon
HC = hydrogen, NZ = nitrogen

Masses, charges and Lennard-Jones parameters

Type ID	Atom	Mass [g mol^{-1}]	σ [Å]	ϵ [kcal mol^{-1}]	charge [e]
1	CT	12.011	3.5	0.066	-0.12
2	CT	12.011	3.5	0.066	-0.18
3	HC	1.008	2.5	0.015	0.06
4	HC	1.008	2.42	0.03	0.115
5	CM	12.011	3.55	0.076	-0.115
6	HC	1.008	2.5	0.03	0.06
7	NZ	14.007	3.2	0.17	-0.56
8	CT	12.011	3.3	0.066	0.04
9	CZ	12.011	3.3	0.066	0.046

Bond coefficients

Type ID	Atoms	r_0 [Å]	k_b [kcal(Åmol)$^{-1}$]
1	CT-HC	1.09	340.0
2	CT-CT	1.529	268.0
3	CT-CM	1.51	317.0
4	CM-HC	1.08	340.0
5	CM-CM	1.34	549.0
6	CT-CZ	1.47	390.0
7	CZ-NZ	1.157	650.0

Angle coefficients

Type ID	Atoms	θ_0	k_θ [kcal mol^{-1}]
1	CT-CM-CM	70.0	124.0
2	CT-CM-HC	35.0	117.0
3	CT-CT-HC	37.5	110.7
4	CT-CT-CT	58.3	112.7
5	CM-CT-HC	35.0	109.5
6	CM-CM-HC	35.0	120.0
7	CM-CT-CT	63.0	111.1
8	HC-CT-HC	33.0	107.8
9	CT-CT-CZ	58.3	112.7
10	CT-CZ-NZ	150.0	180.0
11	HC-CT-CZ	35.0	108.5

Dihedral coefficients - all K_i are [kcal mol^{-1}]

Type ID	Atoms	K_1	K_2	K_3	K_4
1	CT-CM-CM-CT	0.0	14.0	0.0	0.0
2	CT-CM-CM-HC	0.0	14.0	0.0	0.0
3	CT-CT-CT-HC	-0.9	0.0	0.3	0.0
4	CT-CT-CT-CZ	0.0	0.0	0.0	0.0
5	CT-CT-CT-CT	0.7	-0.05	0.2	0.0
6	CM-CM-CT-HC	1.116	0.0	-0.372	0.0
7	CM-CT-CT-HC	-1.098	0.0	0.366	0.0
8	CM-CT-CT-CT	0.7	-0.05	0.2	0.0
9	CM-CM-CT-CT	3.058	0.405	-0.904	0.0
10	HC-CT-CM-HC	-0.954	0.0	0.318	0.0
11	HC-CM-CM-HC	0.0	14.0	0.0	0.0
12	HC-CM-CT-CT	0.0	0.0	0.0	0.0
13	HC-CT-CT-HC	-0.9	0.0	0.3	0.0
14	CT-CT-CZ-NZ	0.0	0.0	0.0	0.0
15	HC-CT-CT-CZ	-1.098	0.0	0.366	0.0
16	HC-CT-CZ-NZ	0.0	0.0	0.0	0.0
17	CZ-CT-CT-CM	0.0	0.0	0.0	0.0
18	CM-CT-CT-CM	0.0	0.0	0.0	0.0

$$
U = \Bigg\{ \overbrace{\frac{1}{2}\sum_{\text{bonds}} k_b \left(r - r_0\right)^2}^{\text{bond terms}} + \overbrace{\frac{1}{2}\sum_{\text{angles}} k_\theta \left(\theta - \theta_0\right)^2}^{\text{angle terms}} +
$$

$$
+ \overbrace{\frac{1}{2}\sum_{\text{dihedrals}} \left\{K_1\left[1+\cos\phi\right] + K_2\left[1-\cos 2\phi\right] + K_3\left[1+\cos 3\phi\right] + K_4\left[1-\cos 4\phi\right]\right\}}^{\text{dihedral terms}} +
$$

$$
+ \overbrace{\sum_{i,j}\left\{ 4\epsilon_{ij}\left[\underbrace{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}}_{\text{repulsive}} - \underbrace{\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}}_{\text{VdW}}\right] + \underbrace{\frac{q_i q_j e^2}{r_{ij}}}_{\text{Coulomb}} \right\} f_{ij}}^{\text{repulsive + VdW + Coulomb terms}}
$$

S2: Volume-temperature plot for T_g

Figure S1 shows the typical volume/temperature curves used to determine the glass transition temperature. For the same HNBR structure with 39% ACN content, two different cross-link fractions are shown, i.e., 0 and 50 %. Figure S1 highlights how cross-links alter the density as well as the glass transition temperature for a given system. At the same temperature, the structure with higher cross-link fraction has a lower volume compared to the same structure with zero cross-links. On the other hand, the intersection point between the rubbery and glassy fit is shifted towards higher temperature, i.e., higher glass transition for more cross-linked systems.

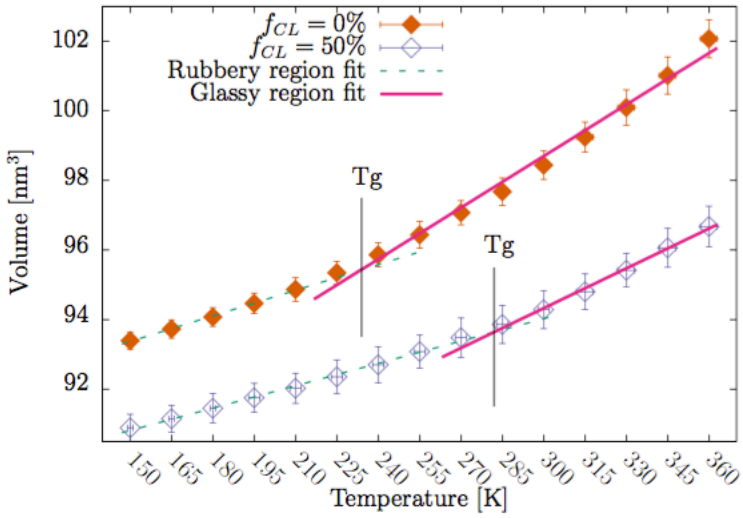

Figure S1: Example of typical volume/temperature curves for HNBR at different cross-link fractions.