

Supplementary Information

**A new insight on the conformation and melt dynamics of hydrogenated
polybutadiene as revealed by computer simulation**

Javier Ramos, Juan F. Vega and Javier Martínez-Salazar

S.1 End-to-end autocorrelation function and Mean-square internal distances

The end-to-end autocorrelation function ($\langle \mathbf{u}(t)\mathbf{u}(0) \rangle$) and the mean square internal distances for the linear polyethylene (LPE) and hydrogenated polybutadienes (PEB2) models are shown in Figure S.1. The $\langle \mathbf{u}(t)\mathbf{u}(0) \rangle$ is fitted with the Kohlrausch-Williams-Watts (KWW) stretch exponential function (dashed lines in Figure S.1.a) as:

$$G(t) = A e^{-\left(t/\tau_{KWW}\right)^\beta}$$

The integration of the KWW curves allows one to get the end-to-end relaxation time (τ_{ACF}) as follows:

$$\tau_{ACF} = \int_0^{\infty} G(t) dt = A \frac{\tau_{KWW}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

, where $\Gamma()$ designates the gamma function. In general, the fitting using the KWW function is very good.

The parameters of the fitting are shown in Table S.1. The relaxation time (τ_{ACF}) increases both with length chain and with the presence of branches. At the same time, the parameter β decreases for branched systems as compared with the linear system of the same molecular length.

Table S.1: Fitting parameters of the end-to-end autocorrelation function to the KWW stretch exponential function.

Model	A	β	τ_{KWW} (ns)	τ_{ACF} (ns)
LPE36	1.00	0.920	0.129	0.135
LPE106	0.98	0.710	1.387	1.698
LPE192	0.98	0.632	5.248	7.256
LPE377	0.99	0.538	27.502	47.991
PBE2_36	1.00	0.907	0.131	0.137
PBE2_106	0.98	0.696	1.390	1.734
PBE2_192	0.98	0.615	5.392	7.705
PBE2_377	0.99	0.524	31.929	58.193

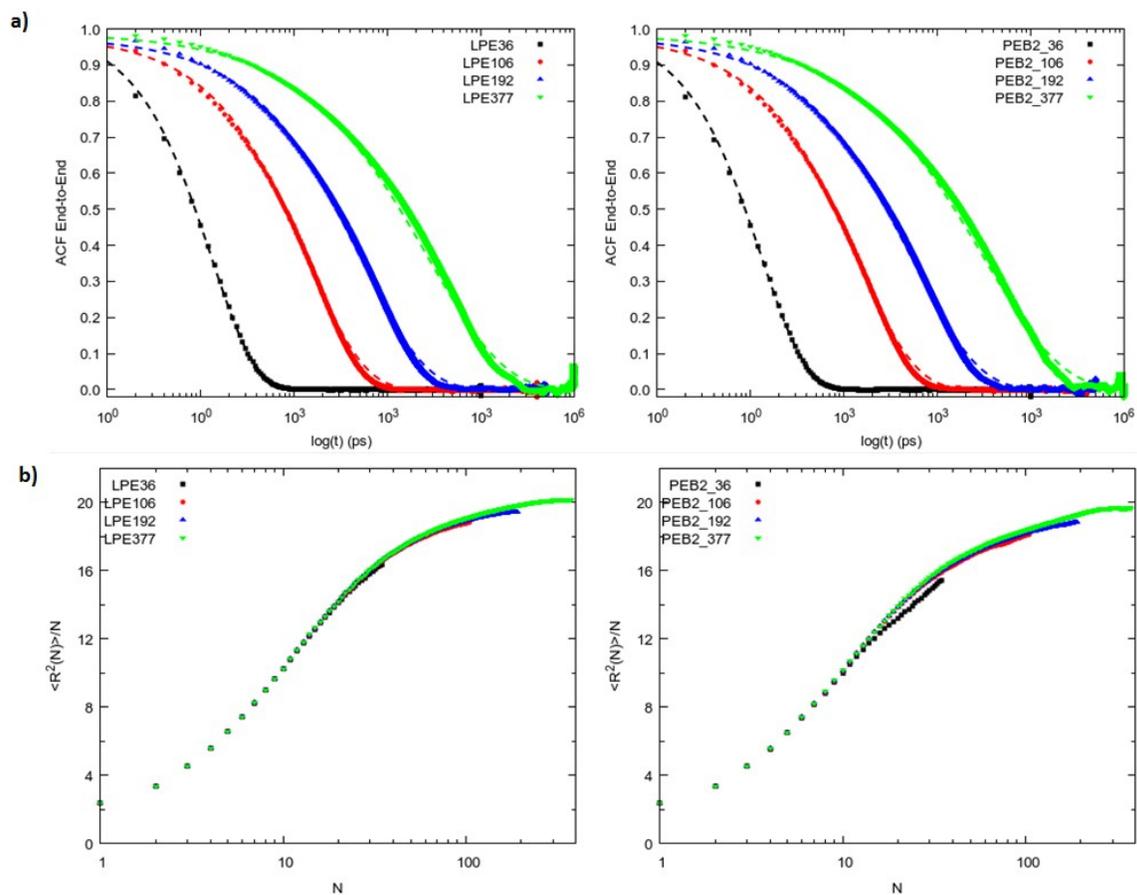


Figure S.1.a) End-to-end autocorrelation function $\langle \mathbf{u}(t)\mathbf{u}(0) \rangle$, where $\mathbf{u}(t)$ is the unit vector at time t along the chain end-to-end vector. The points are the values calculated from the simulations and the dashed lines show the best fit to the KWW equation. **b)** Mean-square internal distances for the linear (LPE) and hydrogenated polybutadiene (PBE2) models.

S.2 Calculated Rouse and reptation relaxation times as well as friction coefficients for LPE and PEB2 simulated systems.

For the two untangled systems, we have directly obtained the Rouse time (τ_R) from the crossover point in the $g_1(t)$ graph as shown in the figure S.2:

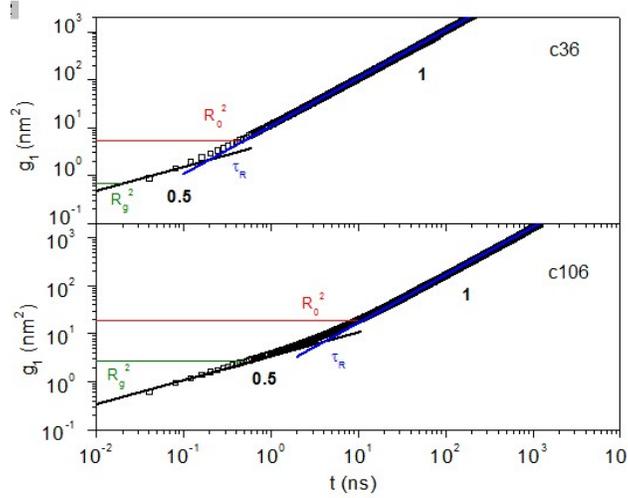


Figure S.2. Mean-squared monomer displacement, $g_1(t)$, for the unentangled PEB2_36 and PEB2_106.

The obtained relaxation times are collected in Table S.2. As it can be seen in this table, the τ_{ACF} is smaller than the corresponding τ_R as discussed by other authors (ref. 25 in the main text).

Using these τ_R values of unentangled systems, it is possible to obtain the friction coefficient by means of the equation:

$$\tau_R = \frac{\zeta N \langle R_0^2 \rangle}{3\pi^2 k_B T} \quad (1)$$

The obtained values are shown in Table S.2. As the coefficient friction is independent of molecular weight above a certain value (see Figure 8 in ref. 29), we have used the value of ζ corresponding to LPE_106 or PEB2_106 to calculate the τ_R for the entangled systems by applying Eq. 1.

Then, the reptation times can be obtained using different approaches: i) τ_d is directly obtained from the $g_1(t)$ graph as $g_1(\tau_d) = \langle R_0^2 \rangle$, ii) from pure reptation model as $\tau_d^0 = 3\tau_e Z^3 = 3\tau_R Z$ (ref.46 main text) and iii) using the contour length fluctuation (CLF) model as $\tau_d^{th} = 3\tau_e Z^3 (1-X Z^{-1/2})^2$, with $X=0.6$ (ref.46 main text). In all cases, the τ_{ACF} is an order of magnitude smaller than the τ_d . This could indicate that the single KWW fitting is not adequate to calculate the reptation times.

As expected, the τ_d^0 (pure reptation model) is higher than τ_d^{th} (taking into account the CLF corrections). The τ_d value obtained directly from the simulations is similar to the τ_d^{th} indicating that the simulations capture the CLF mechanism.

Table S.2: Calculated relaxation times and friction coefficients for all simulated systems.

Sample	M kg·mol ⁻¹	$\langle R_0^2 \rangle$ (nm ²)	Z	τ_R (ns)	τ_d^0 (ns)	τ_d (ns)	τ_d^{th} (ns)	τ_{ACF}^b (ns)	ζ (10 ¹⁰ dyn s cm ⁻¹)
PEB2_36	0.536	5.40	-	0.196 ^a	-	-	-	0.137	2.10 ± 0.19 ^c
PEB2_106	1.547	19.07	-	4.7 ^a	-	-	-	1.73	4.82 ± 0.45 ^c
PEB2_192	2.811	35.86	2.6	15.9 ^d	110 ^e	62.9 ^e	43.7 ^e	7.7	-
PEB2_377	5.493	73.11	5	63.7 ^d	788 ^e	630 ^e	421.6 ^e	58.2	-
LPE_36	0.507	5.73	-	0.168 ^a	-	-	-	0.135	1.69 ± 0.19 ^c
LPE_106	1.489	19.78	-	3.2 ^a	-	-	-	1.70	3.17 ± 0.39 ^c
LPE_192	2.695	37.14	3.4	9.8 ^d	94.3 ^e	53.6 ^e	42.9 ^e	7.3	-
LPE_377	5.290	75.66	6.6	39.2 ^d	690 ^e	502 ^e	405.3 ^e	48.0	-

^a Rouse time obtained directly from the crossover point in the $g_1(t)$ vs t graph (see Figure 3 in the main text)

^b Longest relaxation time from KWW equation (see S.1)

^c The τ_R values of unentangled systems have used to calculate the coefficient friction (ζ) by applying $\tau_R = \zeta N \langle R_0^2 \rangle / 3\pi^2 k_B T$ (ref.46 main text)

^d Using the ζ corresponding to LPE_106 or PEB2_106, one can calculate the τ_R for the entangled systems by applying the above equation.

^e The reptation times are obtained as: i) τ_d is directly obtained from the $g_1(t)$ graph as $g_1(\tau_d) = \langle R_0^2 \rangle$, ii) from pure reptation model as $\tau_d^0 = 3\tau_e Z^3 = 3\tau_R Z$ (ref.46 main text) and iii) using the contour length fluctuation (CLF) model as $\tau_d^{th} = 3\tau_e Z^3 (1-X Z^{-1/2})^2$, with $X=0.6$ (ref.46 main text).

S.3 Characteristic ratio (C_n) for the linear polyethylene (LPE) and hydrogenated polybutadiene (PEB2) as a function of the molecular length.

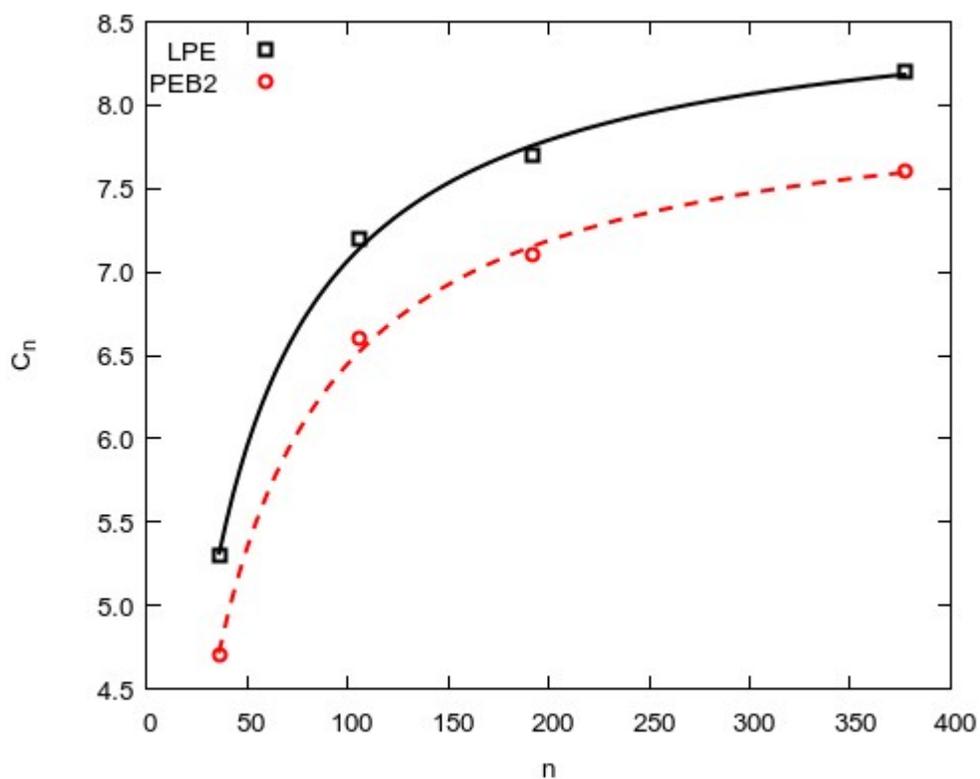


Figure S.3. Characteristic ratio (C_n) for the linear polyethylene (LPE) and hydrogenated polybutadiene (PEB2) as a function of the molecular length (n). For a nice explanation of characteristic ratio as an indicator of the chain stiffness see, for example, Bicerano J., Computational and Theoretical Polymer Science, 8, 9-13, 1998.

S.4 Mean-squared monomer displacement for the simulated and PEB2 models.

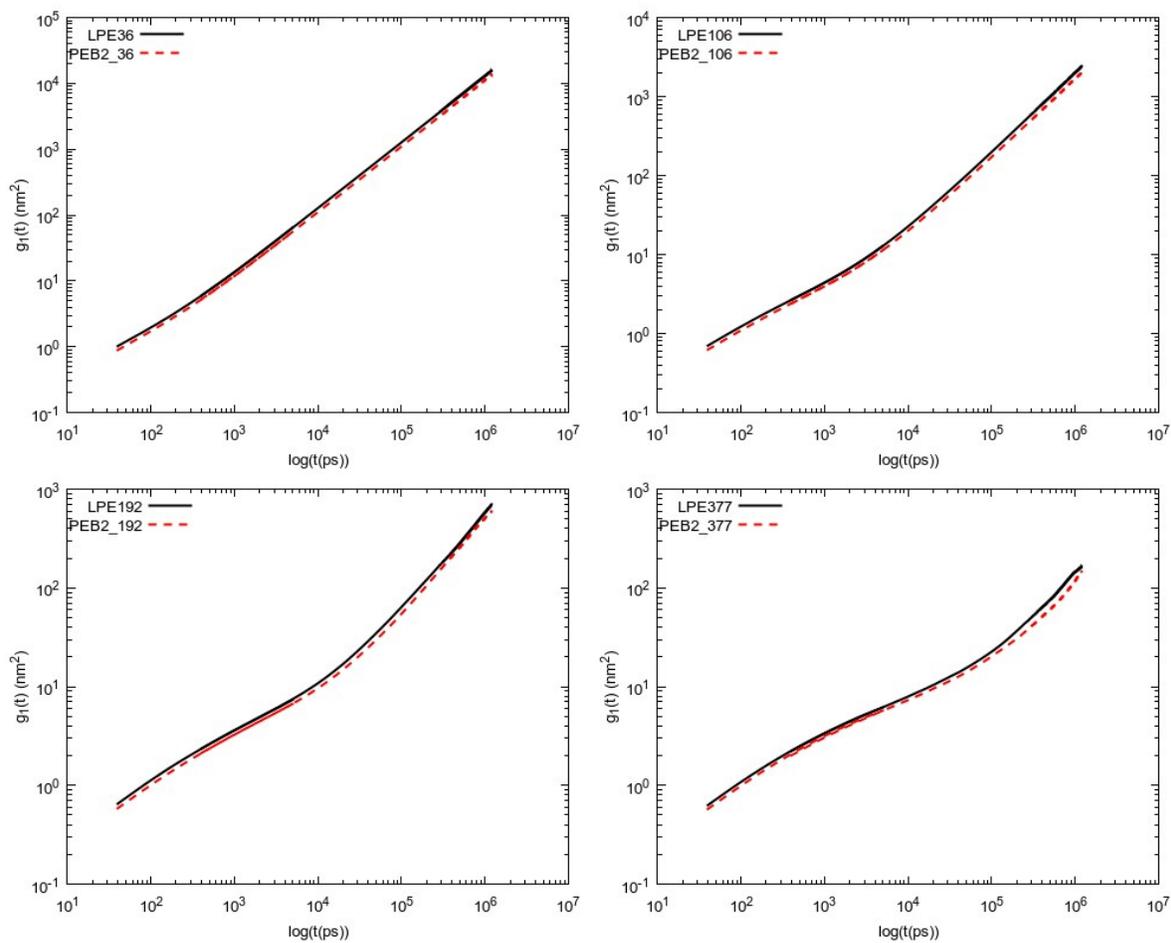


Figure S.4. Mean-squared monomer displacement, $g_1(t)$, for the simulated LPE (solid lines) and PEB2 (dashed lines) samples at 509 K. The ethyl branches seem to produce a slow-down of the segmental dynamics in all cases.

S.5 Intermolecular radial pair distribution functions, $g_{\text{inter}}(r)$.

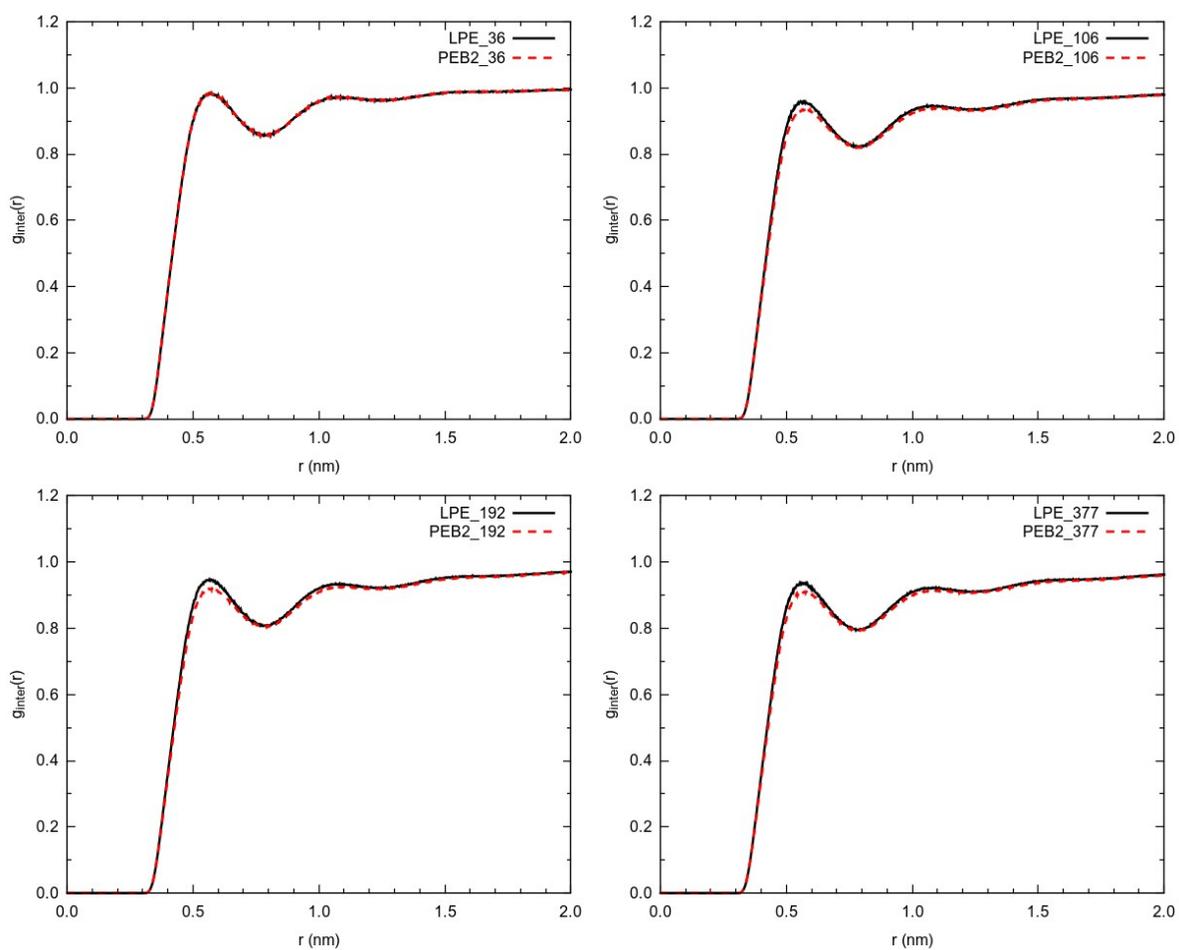


Figure S.5. Intermolecular radial pair distribution function of the simulated LPE (black solid lines) and PEB2 (red dashed lines) samples at 509 K.