Supplementary Information

Effect of Short-Chain Branching on Interfacial Polymer Structure and Dynamics under Shear Flow

Sohdam Jeong,† Jun Mo Kim,† Soowon Cho, and Chunggi Baig*  
School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), UNIST-gil 50, Eonyang-eup, Ulju-gun, Ulsan 689-798, South Korea

†These authors contributed equally to this work.

*Author to whom correspondence should be addressed.

E-mail: cbaig@unist.ac.kr.

Tel: +82-52-217-2538.

Fax: +82-52-217-2649
Materials and Methods

The modified $p$-SLLOD equations of motion with a Nosé-Hoover thermostat for confined systems have the following expressions:

\[
\frac{\dot{r}_i}{m_i} = \frac{p_i - m_i \dot{r}_i \cdot \nabla u}{m_i},
\]

\[
\dot{p}_i = F_i(r) - p_i \cdot \nabla u - m_i \dot{r}_i \cdot \nabla u \cdot \nabla u - \frac{p_i}{Q} - \frac{p_s}{Q} (m_i \dot{r}_i \cdot \nabla u - m_i U(r)),
\]

\[
\dot{s} = \frac{p_s}{Q}, \quad \dot{p}_s = F_s(p_s), \quad Q = D N k_B T \tau_t^2.
\]

where $r_i$, $p_i$, and $F_i$ indicate the position, (nominal) peculiar momentum, and force vector of atom $i$ of the mass $m_i$. The $s$ and $p_s$ are position-like and momentum-like variables, respectively, of the Nosé-Hoover thermostat. The $Q$ represents the thermostat mass parameter, for which $D$, $N$, and $\tau_t$ refer the dimensionality of the system, the total number of atoms, and the thermostat relaxation time parameter, respectively. The $\tau_t$ was set equal to 0.24 ps in all simulations. The $\nabla u$, homogeneous velocity gradient tensor, is expressed as

\[
\nabla u = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}
\]

where $\dot{\gamma}$ is the shear rate. The streaming velocity $U(r_i)$ at atomic position $r_i$ was obtained from a 5th-order polynomial fit in every MD step throughout the total (bulk plus interfacial) region. The real peculiar momentum $p_i^{\text{real}}$ of each atom was then calculated by removing the streaming velocity at its position from its laboratory momentum $p_i' = p_i + m_i r_i \cdot \nabla u$:

\[
p_i^{\text{real}} = p_i' - m_i U(r_i)
\]
In the TraPPE model, nonbonded atomic interactions including intra-, intermolecular interaction were modeled by a pairwise 6-12 Lennard-Jones (LJ) potential:

\[
U_{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] 
\]

(4)

where \( \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \) and \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) were followed the standard Lorentz-Berthelot mixing rules between atomistic units \( i \) and \( j \). The LJ parameters \( \sigma_{CH}, \sigma_{CH_2}, \) and \( \sigma_{CH_3} \) were set equal to 4.68 Å, 3.95 Å, and 3.75 Å, respectively, and the energy parameters \( \varepsilon_{CH}/k_B, \varepsilon_{CH_2}/k_B, \) and \( \varepsilon_{CH_3}/k_B \) equal to 10 K, 46 K, and 98 K, respectively. The \( r_c = 2.5 \sigma_{ij} \) is a cut-off distance for both atom-atom and atom-wall. In our confined system simulations, wall atoms only interact with fluid atoms, not with each wall atoms. The bonded atomic interactions involving bond-stretching \( (U_{\text{str}}) \), bond-bending \( (U_{\text{ben}}) \) and bond-torsional \( (U_{\text{tor}}) \) were described by

\[
U_{\text{str}}(l) = \frac{k_{\text{str}}}{2} (l - l_{\text{eq}})^2, 
\]

(5)

\[
U_{\text{ben}}(\theta) = \frac{k_{\text{ben}}}{2} (\theta - \theta_{\text{eq}})^2, 
\]

(6)

\[
U_{\text{tor}}(\phi) = \sum_{m=0}^{3} a_m (\cos \phi)^m 
\]

(7)

where, for bond-stretching interaction, the bond-stretching constant is \( k_{\text{str}}/k_B = 452,900 \text{ K/Å}^2 \) and the equilibrium bond length \( l_{\text{eq}} = 1.54 \text{ Å} \). The bond-bending parameter \( k_\theta \) is equal to 122.188 kcal/(mol rad²), and the equilibrium bending angle \( \theta_{\text{eq}} = 114^\circ \) for CH₃–CH₂–CH₃ (with \( x \) and \( y \) equal to 2 or 3), \( \theta_{\text{eq}} = 112^\circ \) for CH₃–CH–CH₃, and \( \theta_{\text{eq}} = 109.47^\circ \) for CH₃–C–CH₃. The
bond-torsional parameters are such that (a) $a_0 = 2.0071$, $a_1 = 4.0122$, $a_2 = 0.27105$, $a_3 = -6.2895$ (kcal/mol) for CH$_x$–CH$_2$–CH$_2$–CH$_y$, (b) $a_0 = 0.78542$, $a_1 = 1.7787$, $a_2 = 0.44454$, $a_3 = -3.5076$ (kcal/mol) for CH$_x$–CH$_2$–CH–CH$_y$, and (c) $a_0 = 0.91670$, $a_1 = 2.7503$, $a_2 = 0$, $a_3 = -3.6665$ (kcal/mol) for CH$_x$–CH$_2$–C–CH$_y$ [note that here $\phi = 0$ represents the (most stable) trans-conformation, whereas it refers to the cis-conformation]. The LJ energy and size parameters $\varepsilon$ and $\sigma$ are respectively equal to 0.19475 kcal/mol and 3.75 Å for the CH$_3$ united-atom, 0.09141 kcal/mol and 3.95 Å for the CH$_2$ united-atom, and 0.01987 kcal/mol and 4.68 Å for the CH united-atom. For bond-bending interaction, the bond-bending constant is $k_{\text{ben}}/k_B = 62,500$ K/rad$^2$ and the equilibrium bond angle $\theta_{\text{eq}} = 114^\circ$. 
**Figure S1.** Characteristic time scale ($t_{wag}$) of the attachment-detachment wagging motions of interfacial chains in the intermediate flow regime for the simulated linear and SCB polyethylene melts, estimated by fitting with a sine function the temporal variations of the average $y$-position for the center-of-mass of the non-adsorbed parts ($y_{nadv}$) presented in Fig. 3b in the main text.
Figure S2. Average tumbling time ($t_{\text{tumb}}$) over all the chains of system for the linear and SCB polyethylene melts as a function of $Wi$, based on the time correlation function $\langle R_x(t)R_y(0) \rangle$ between the $x$- and $y$- components of the chain end-to-end vector $\mathbf{R}$. We note that due to the frequent movements of the interfacial chains between interfacial and bulk regions in the confined system, it is not feasible to extract the tumbling times only for the interfacial chains. As expected, $t_{\text{tumb}}$ decreases with increasing $Wi$ number for both melts. Interestingly, despite that the characteristic rotation and tumbling mechanisms of interfacial chains are different between the two systems (i.e., hairpin tumbling for the linear polymer vs. hairpin tumbling and rolling for the SCB polymer), $t_{\text{tumb}}$ is found to be very similar to each other at the same $Wi$ number.
**Supplementary Movies**

**Movie S1**: Tumbling dynamics of the interfacial linear polymer

**Movie S2**: Head-rolling tumbling dynamics of the interfacial SCB polymer

**Movie S3**: Tail-rolling tumbling dynamics of the interfacial SCB polymer