Structural and Dynamical Characteristics of Short-Chain Branched Ring Polymer Melts at Interface under Shear Flow

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Simulation Methodology

The well-known Transferable Potentials for Phase Equilibria (TraPPE) united-atom model was adopted in the simulations [1]. In the TraPPE model, nonbonded intra- and intermolecular interaction were modeled by a pairwise 6-12 Lennard-Jones (LJ) potential:

$$U_{LJ}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]$$  (1)

where $\epsilon/k_B$ for the CH, CH$_2$, and CH$_3$ are 10 K, 46 K, and 98K, respectively, and $\sigma$ for the CH, CH$_2$, and CH$_3$ are 4.68 Å, 3.95 Å, and 3.75 Å, respectively, where $k_B$ denotes the Boltzmann constant. The cut-off distance for both atom-atom and atom-wall is 2.5 $\sigma$. The three bonded (bond-stretching, bond-bending, and bond-torsional) interactions are modeled by the following potentials:

$$U_{\text{stretching}}(l) = \frac{k_l}{2} (l - l_{eq})^2$$  (2)

$$U_{\text{bending}}(\theta) = \frac{k_{\theta m}}{2} (\theta - \theta_{eq})^2$$  (3)

$$U_{\text{torsional}}(\phi) = \sum_{m=0}^{\infty} a_m \cos^m \phi$$  (4)

where the bond-stretching constant is $k_l/k_B = 452,900$ K/Å and the equilibrium bond length $l_{eq} = 1.54$ Å. The bond-bending parameter $k_{\theta m}$ is equal to 62.500 K/Å$^2$ and the equilibrium bending angle $\theta_{eq}$ is 114°, 112°, and 109.47° for CH$_3$-CH$_2$-CH$_2$, CH$_3$-CH-CH$_2$, and CH$_3$-C-CH$_2$, respectively, where $x$ and $y$ are equal to 2 or 3. The bond-torsional parameters are such that (i) $a_0 = 1010$ K, $a_1 = 1990$ K, $a_2 = 136.4$, and $a_3 = -3165$K for CH$_3$-CH$_2$-CH$_2$-CH$_2$, (ii) $a_0 = 395.2$ K, $a_1 = 895.1$ K, $a_2 = 223.7$ K, and $a_3 = -1765.2$ K for CH$_3$-CH$_2$-CH-CH$_2$, and (iii) $a_0 = 461.3$ K, $a_1 = 1384.1$ K, $a_2 = 0$ K, and $a_3 = -1845.2$ K for CH$_3$-CH$_3$-CH$_2$. [note that here $\phi = 0$ indicates the (most stable) trans-conformation, whereas $\phi = 180^\circ$ refers to the cis-conformation].

The simulation systems were confined by rigid simple cubic lattice walls where the lattice parameter of the simple cubic wall was set equal to $\sigma_w = 1.33 \sigma$ where $\sigma$ is $\sigma_{CH_3}$ [2]. The LJ energy parameter of wall atoms in all PE systems was set as $\omega/k_B = 939$ K, which is comparable to that of a mica surface (~200-400 ml/m$^2$) [3]. The simulation systems were confined by rigid simple cubic lattice walls composed of 676, 1352, and 2028 atoms for each of the C$_{12}H_{25}$ linear, C$_{12}H_{25}$ ring, and C$_{17}H_{38}$ short-chain branched (SCB) linear PE systems, and 1224, 2448, and 3672 atoms for the C$_{17}H_{38}$ SCB ring PE system. Each wall atom was kept fixed in its lattice site during the simulations. The interaction parameters between wall atom $w$ and polymer atom $f$ were specified as $\omega_{wf} = (\omega_w \sigma_w)^{12}$ and $\sigma_{wf} = (\sigma_w + \sigma_f)/2$. The cut-off distance of the LJ polymer-wall interaction was set as 2.5$\sigma_{wf}$. Therefore, the polymer-wall interaction can be active up to two layers at most. As such, each top and bottom wall boundary was set by two layered simple cubic lattice walls for all PE confined systems in this study.

The atomistic nonequilibrium molecular dynamics (NEMD) simulations were executed with the $p$-SLLOD algorithm with a Nosé-Hoover thermostat [4-7].
The real peculiar momentum $p_i^{\text{real}}$ of each atom was then calculated by subtracting the streaming velocity at its position from its laboratory momentum:

$$p_i^{\text{real}} = p_i + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} - m_i \mathbf{U} (\mathbf{r}_i)$$

(6)

The $\nabla \mathbf{u}$, homogeneous velocity gradient tensor, is expressed as

$$\nabla \mathbf{u} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

(7)

where $\dot{\gamma}$ is the shear rate.

The bulk polymer configurations were initially constructed via an efficient Monte Carlo algorithm in the Material Studio (Accelrys Inc.) software package subsequently subjected to the energy minimization and pre-equilibration procedures. Then, simple cubic lattice walls were placed at the top and bottom boundary of the system in the confining ($y$-)direction to accommodate the initial bulk polymer system. We then applied isothermal-isobaric (NPT) molecular dynamics simulations to the confined system for a sufficiently long time to attain the equilibrium density of the system at $P = 1$ atm and $T = 450$ K.

References