

Supplementary Material (ESI) for Soft Matter
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Projection of atomistic simulation data for the dynamics of entangled polymers onto the tube theory:

Calculation of the segment survival probability function and comparison with modern tube models

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Supporting Information

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In this supplementary material we present the details of the potential models employed in our molecular dynamics (MD) simulations for polyethylene (PE) and *cis*-1,4 and *trans*-1,4 polybutadiene (PB) melts. The reader is also directed to Refs S1-S3 for additional information.

1. Potential model for polyethylene melts

All MD simulations of PE melts have been conducted in isobaric-isothermal (*NPT*) statistical ensemble at $T=450$ K and $P=1$ atm using the LAMMPS (large-scale atomic/molecular massively parallel simulator) software.^{S4} For the numerical integration of the equations of motion, the reversible Reference System Propagator Algorithm (*r*-RESPA)^{S5} was employed with the small integration time step set as equal to 1 fs and the large one to 5 fs. The Nosé-Hoover thermostat^{S6} and the Andersen barostat^{S7} were used to control the temperature and the pressure, respectively. A standard united-atom description is used, according to which all hydrogen atoms attached to a carbon atom (e.g., CH₂ and CH₃) are lumped into a single spherically symmetric interaction site.

All intramolecular interactions between sites separated by more than three bonds along the chain as well as all intermolecular ones between sites belonging to different chains are described via a 12-6 Lennard-Jones (LJ) potential:

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (\text{S1})$$

with ε and σ for the CH₂ and CH₃ being taken from the well-known TraPPE model:^{S8} $\varepsilon=0.09131$ kcal.mol⁻¹ and $\sigma=3.95$ Å. Following Nath et al.,^{S9} bond lengths are allowed to fluctuate via a harmonic potential:

$$V_{stretching}(l) = \frac{1}{2}k_l(l-l_0)^2, \quad (\text{S2})$$

where $l_0 = 1.54$ Å and $k_l=191.55$ kcal mol⁻¹ Å⁻². Bond bending interactions obey the Van der Ploeg-Berendsen^{S10} bending potential:

$$V_{bending}(\theta) = \frac{1}{2}k_\theta(\theta-\theta_0)^2, \quad (\text{S3})$$

where $\theta_0 = 114^\circ$ and $k_\theta = 124.06 \text{ kcal mol}^{-1} \text{ rad}^{-2}$. Finally, the torsional potential employed follows Toxvaerd:^{S11}

$$V_{\text{torsional}}(\phi) = \sum_{n=0}^8 c_n \cos^n(\phi), \quad (\text{S4})$$

with $c_0 = 1.9869$, $c_1 = 4.2281$, $c_2 = -0.6015$, $c_3 = -7.1698$, $c_4 = 4.4206$, $c_5 = 3.9025$, $c_6 = -8.9107$, $c_7 = -3.4460$ and $c_8 = 5.5917$ (all in units of kcal mol^{-1}).

2. Potential model for *cis*-1,4 and *trans*-1,4 polybutadiene melts

All MD simulations of *cis*-1,4 and *trans*-1,4 PB melts have also been conducted in the *NPT* statistical ensemble at $T = 413 \text{ K}$ and $P = 1 \text{ atm}$ using the LAMMPS (large-scale atomic/molecular massively parallel simulator) software.^{S4} The *r*-RESPA^{S5} was employed with the small integration time step set as equal to 2 fs and the long to 5 fs. The Nosé-Hoover thermostat and barostat^{S6} were used to control the temperature and the pressure, respectively. A united-atom description (e.g., CH, CH₂, and CH₃) was employed.

All intramolecular interactions between sites separated by more than three bonds along the chain as well as all intermolecular ones are described via a 12-6 Lennard-Jones potential (eq S1) with ϵ and σ being taken from the work of Smith and Paul^{S12} [see (a) in Table S1]. Bond lengths fluctuate via the harmonic potential (eq S2) where the values of l_0 and k_l are obtained from Gee and Boyd^{S13} and the bond angles again follow the harmonic potential (eq S3) with the values of θ_0 and k_θ obtained from Gee and Boyd^{S13}, which are the same as in Smith and Paul^{S12} [see (b) in Table S1]. Finally, the torsional potential is obtained from Smith and Paul^{S12}

$$V_{\text{torsional}}(\phi) = \frac{1}{2} \sum_{n=1}^6 c_n (1 - \cos(n\phi)), \quad (\text{S5})$$

where the parameters c_n are given in Table S1.

Table S1: Values of the Force Field parameters for the simulation of PB

(a) *bond-stretching*

| types | k_l ($\text{kcal.mol}^{-1} \cdot \text{\AA}^{-2}$) | l_0 (\AA) |
|----------------------------------|--|------------------------|
| CH ₂ -CH ₂ | 158.5 | 1.54 |
| CH ₂ -CH | 183.8 | 1.50 |

| | | |
|-------|-------|------|
| CH=CH | 246.9 | 1.34 |
|-------|-------|------|

(b) *bond-bending*

| types | k_θ (kcal.mol ⁻¹ . Å ⁻²) | θ_0 (°) |
|--------------------------------------|--|----------------|
| CH ₂ -CH ₂ -CH | 115 | 111.65 |
| CH ₂ -CH | 89.4 | 125.89 |

(c) *bond-torsional*

| types | k_1 (kcal.mol ⁻¹) | k_2 (kcal.mol ⁻¹) | k_3 (kcal.mol ⁻¹) | k_4 (kcal.mol ⁻¹) | k_5 (kcal.mol ⁻¹) | k_6 (kcal.mol ⁻¹) |
|---|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| CH ₂ -CH=CH-CH ₂ | | 24.2 | | | | |
| CH ₂ -CH ₂ -CH=CH | 1.033 | -0.472 | 0.554 | 0.263 | 0.346 | 0.164 |
| CH-CH ₂ -CH ₂ -CH | -0.888 | -0.619 | -3.639 | -0.066 | -0.247 | -0.190 |

(d) *non-bonded Lennard-Jones*

| types | ϵ (kcal.mol ⁻¹) | σ (Å) |
|----------------------------------|--------------------------------------|--------------|
| CH ₂ -CH ₂ | 0.0963 | 4.500 |
| CH ₂ -CH | 0.1000 | 3.800 |
| CH=CH | 0.1015 | 4.257 |

The initial configuration in all the simulations of PE and PB systems was obtained from the Cerius² software^{S14} and was then subjected to a minimization process to minimize the total energy of the initial configuration. Constant-volume *NVT* and constant-pressure *NPT* Monte Carlo simulations (e.g. ref S15) were subsequently employed to further equilibrate the initial system configuration; the resulting configuration was then used in the MD simulations in this study. This initial system configuration was carefully chosen to have a uniform chain-length distribution, a density close to the average melt density of the simulated system at the temperature and pressure of interest, and a mean-square chain end-to-end distance $\langle R^2 \rangle$ close to the real average value of the simulated system.¹⁵ Conventional periodic boundary conditions were applied in all three directions (x, y, z).¹⁶

References and Notes

- (S1) V. A. Harmandaris, V. G. Mavrantzas and D. N. Theodorou, *Macromolecules*, 2000, **33**, 8062.
 (S2) N. Ch. Karayiannis and V. G. Mavrantzas, *Macromolecules*, 2005, **38**, 8593.

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This journal is (c) The Royal Society of Chemistry 2010

- (S3) G. Tsolou, V. G. Mavrantzas and D. N. Theodorou, *Macromolecules*, 2005, **38**, 1478; G. Tsolou, V. A. Harmandaris and V. G. Mavrantzas, *Macromol. Theory Simul.*, 2006, **15**, 381 (note that the values of k_{str} reported in Table 1 of the *Macromolecules* paper are in error and the corrected values are presented in Table 1 of the *Macromol. Theory Simul.* paper)
- (S4) S. J. Plimton, *J. Comput. Phys.*, 1995, **117**, 1.
- (S5) M. Tuckerman, B. J. Berne and G. J. Martyna, *J. Chem. Phys.*, 1992, **97**, 1990; G. J. Martyna, M. Tuckerman, D. J. Tobias and M. L. Klein, *Mol. Phys.*, 1996, **87**, 1117.
- (S6) S. Nosé, *Prog. Theor. Phys. Suppl.*, 1991, **103**, 1; W. G. Hoover, *Phys. Rev. A*, 1986, **31**, 1695.
- (S7) H. C. Andersen, *J. Chem. Phys.*, 1980, **72**, 2384.
- (S8) M. G. Martin and J. I. Siepmann, *J. Phys. Chem. B.*, 1998, **102**, 2569.
- (S9) S. K. Nath, F. A. Escobedo and J. J. de Pablo, *J. Chem. Phys.*, 1998, **108**, 9905; S. K. Nath and R. Khare, *J. Chem. Phys.*, 2001, **115**, 10837.
- (S10) P. Van der Ploeg and H. J. C. Berendsen, *J. Chem. Phys.*, 1982, **76**, 3271.
- (S11) S. Toxvaerd, *J. Chem. Phys.*, 1997, **107**, 5197.
- (S12) G. D. Smith and W. Paul, *J. Phys. Chem. A*, 1998, **102**, 1200.
- (S13) R. H. Gee and R. H. Boyd, *J. Chem. Phys.*, 1994, **101**, 8028.
- (S14) www.accelrys.com/ceius2/
- (S15) P. Gestoso, E. Nicol, M. Doxastakis and D. N. Theodorou, *Macromolecules.*, 2003, **36**, 6925.
- (S16) M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, Oxford, 1987.