

Supplementary information for “Multiscale Modeling of Soft Matter: Scaling of Dynamics”

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Technical details for section 4 “Specific applications and discussion: tacticity, additives” are given in the following

0.0.1 Atomistic simulations. For the atomistic simulations performed in this work we used an all-atom (AA) model for polystyrene (PS).¹ In the all-atom description each PS monomer is described by 16 atoms. Periodic boundary conditions and a cutoff distance of 1 nm for nonbonded interactions were used. Cutoff corrections were applied to energy and pressure using standard analytical expressions that assume a uniform density beyond the cutoff.² All bond lengths are constrained using the LINCS method.³ The integration time step was 1 fs.

All-atom PS 10-mer melts were simulated under isothermal-isobaric (NpT) conditions at a temperature of 503 K and 1 atm using the Berendsen thermostat (coupling time 0.2 ps) and barostat (coupling time 2 ps).⁴ Melts of 10-mers were simulated for atactic, isotactic, and syndiotactic tacticity. The atactic chains use different random sequences of diads with a probability $p = 0.5$ meso diads. Each system consists of 56 chains of 10 monomers.

The mixed system of ethylbenzene and polystyrene was simulated under isothermal-isochoic (NVT) conditions at a temperature of 503 K and at a density of 910 kg/m³. For the mixed EB/PS systems we used the velocity rescaling thermostat⁵ (coupling time 0.2 ps) independently for PS and EB. The studied system consists of 24 atactic PS chains with a length of 96 monomers ($M_W = 9984$ g/mol) and an EB weight fraction w_{EB} of 0.1 (256 molecules).

0.0.2 Coarse-grained simulations. For the coarse-grained simulations presented in this work a recently developed coarse-grained model for polystyrene was used.⁶ The development of the CG model is based on the all-atom force field¹, which is used in this work as well. Bonded and nonbonded interaction potentials were developed separately. The model reproduces the density of the all-atom model at ambient pressure and the local packing of chain segments in melts of 10-mers in a temperature range between 400 K and above 530 K. Special attention was paid to the development of bonded potentials, which describe local distributions cor-

rectly for stereoregular as well as for atactic systems and take into account correlations between neighboring CG degrees of freedom. In that way chain dimensions are in agreement with atomistic simulations on all length scales beyond the CG bead size.

The CG model uses a 2:1 mapping scheme, representing each PS monomer by two CG beads, in contrast to 16 atoms in the all-atom description. Staying still close to the chemical structure of the polymer allows to reintroduce chemical details into the coarse-grained systems (“inverse mapping”). By that one gets well-equilibrated atomistic conformations, while the actual equilibration of the long polymer chains happens on the CG level. This method was used to obtain initial atomistic conformations of mixed systems of long PS chains and ethylbenzene additives.

The coarse-grained PS 10-mer melts consist of 384 chains and were set up with three different tacticities, using the same random sequences for the diads in the atactic system as in the atomistic atactic system. CG simulations were performed under isothermal-isochoic (NVT) conditions at a temperature of 503 K and at the density of the corresponding all-atomistic systems using the velocity rescaling thermostat (coupling time 0.2 ps).⁵ The 10-mer melts were simulated for 75 ns, using an integration time step of 3 fs.

The CG mixed system of EB and PS has the same number of molecules as the corresponding atomistic system. It consists of 24 atactic PS chains with a length of 96 monomers ($M_W = 9984$ g/mol) and an EB weight fraction w_{EB} of 0.1 (256 molecules). The EB molecules in the CG simulation were modeled by the beads also used for PS and the same nonbonded potentials. The system was simulated under isothermal-isobaric (NpT) conditions at a temperature of 503 K and 1 atm using the velocity rescaling thermostat (coupling time 0.5 ps) independently for PS and EB and the Berendsen barostat (coupling time 5 ps). The mixed EB/PS system was simulated for 96 ns, using an integration time step of 4 fs.

In all CG simulations periodic boundary conditions and a cutoff of 1 nm for nonbonded interactions were used. The motion of the center of mass of the whole system was subtracted in regular intervals. The simulations in this work were performed with the GROMACS package⁷ and the CG tools of the VOTCA package.⁸

References

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