

Electronic Supplementary Information

Controlled production of patchy particles from the combined effects of nanoprecipitation and vitrification

Nannan Li,[†] Arash Nikoubashman,^{*,‡} and Athanassios Z. Panagiotopoulos^{*,†}

[†]*Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, USA*

[‡]*Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany*

E-mail: anikouba@uni-mainz.de; azp@princeton.edu

Glass transition temperature calculations for polymers A and B

We performed MD simulations to determine the glass transition temperatures, T_g , of polymers A and B, both in bulk and in aggregates under poor solvent conditions. The simulations were carried out at constant temperature and constant pressure $p = 0$.

To calculate T_g in the bulk, we study the specific volume, v , and the Lennard-Jones energy per bead between non-bonded monomers, E_{NB} , during cooling, and T_g is indicated by a change of slope in the temperature dependence of these quantities. The system contained 500 polymer chains with $N = 23$ beads. The system was initially equilibrated at $T = 2.0$, and T was then lowered every 50,000 MD steps by 0.02 until the final value of T was reached. From Figure S1, it is clear that both v and E_{NB} indicate $T_{g,A} = 1.3$ for polymer A, and $T_{g,B} = 0.9$ for polymer B.

To verify that aggregates of polymer A and B undergo glass transition at the same temperatures as in the bulk, we prepared a cubic box with an edge length of 30σ which contained an aggregate of 64 polymer chains and 17,820 sol-

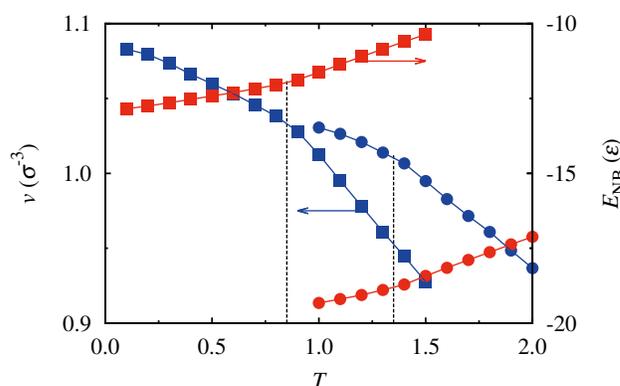


Figure S1: Specific volume, v , and Lennard-Jones energy per bead between non-bonded monomers, E_{NB} , of polymers in bulk *vs.* temperature, T . The circles represent polymer type A, and the squares represent polymer type B. The positions of the kinks indicate that $T_{g,A} = 1.3$, and $T_{g,B} = 0.9$.

vent particles in poor solvent conditions, *i.e.*, $\lambda = 0.5$. Figure S2 shows the Lennard-Jones energy per bead between non-bonded monomers, E_{NB} , *vs.* T upon cooling, and a kink can be found at $T = 1.3$ and 0.9 for polymer A and B, respectively.

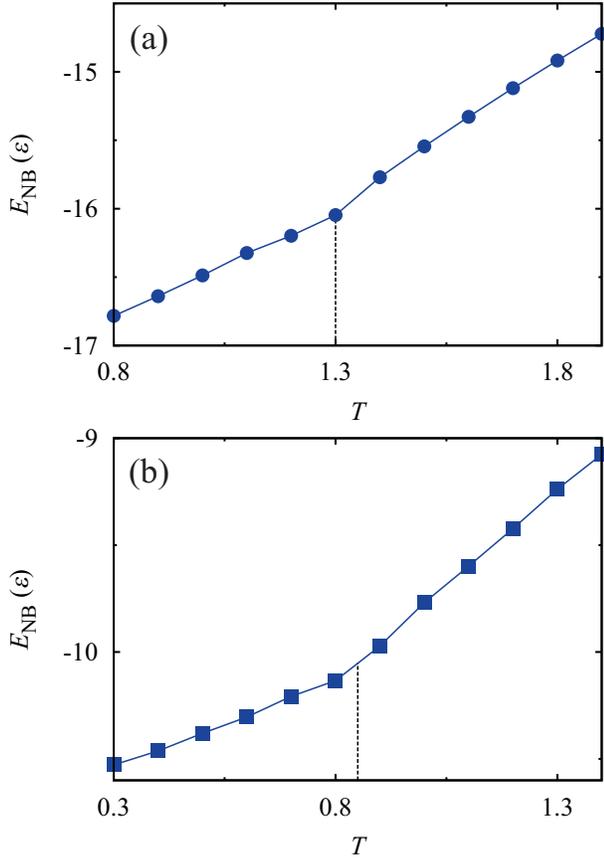


Figure S2: Dependence of Lennard-Jones energy per bead between non-bonded monomers, E_{NB} , of an aggregate in poor solvent conditions on temperature, T , for (a) polymer A and (b) polymer B. The positions of the kinks indicate that $T_{g,A} = 1.3$, and $T_{g,B} = 0.9$.