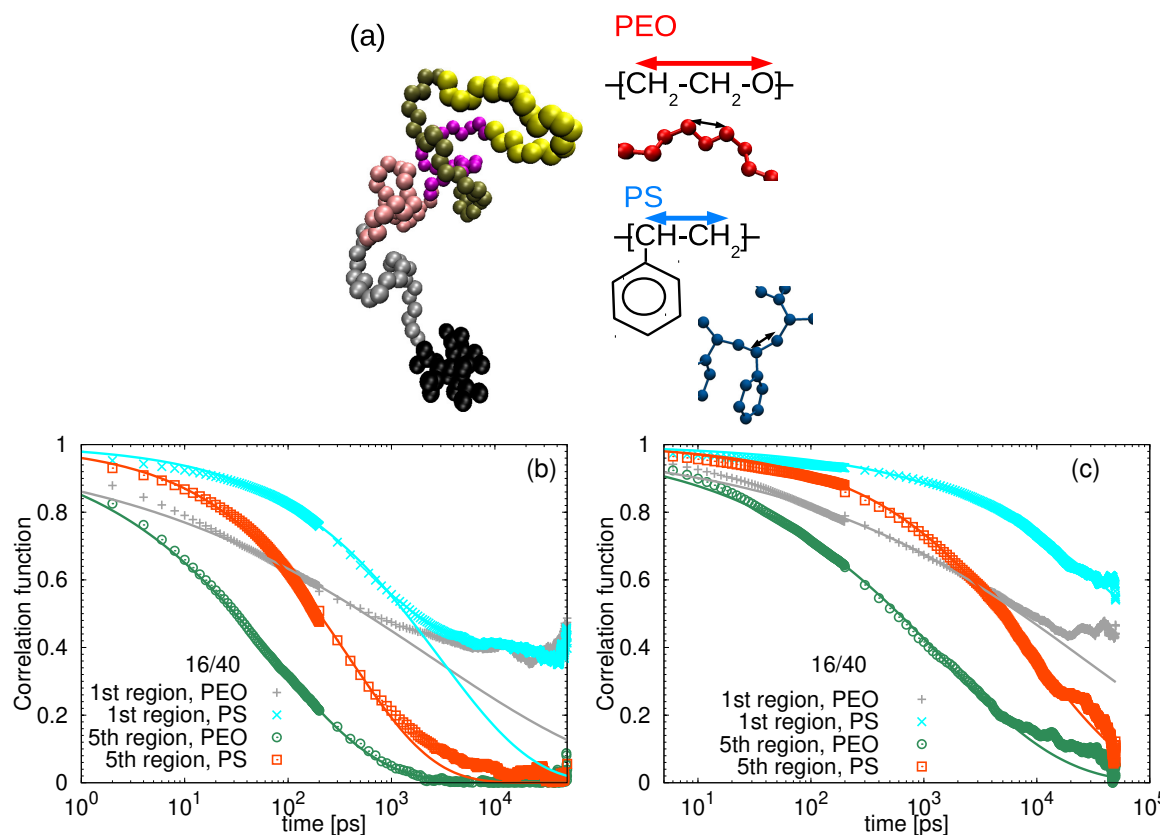


## SUPPLEMENTARY INFORMATION

### Spatio-temporal Heterogeneities in Nanosegregated Single-molecule Polymeric Nanoparticles

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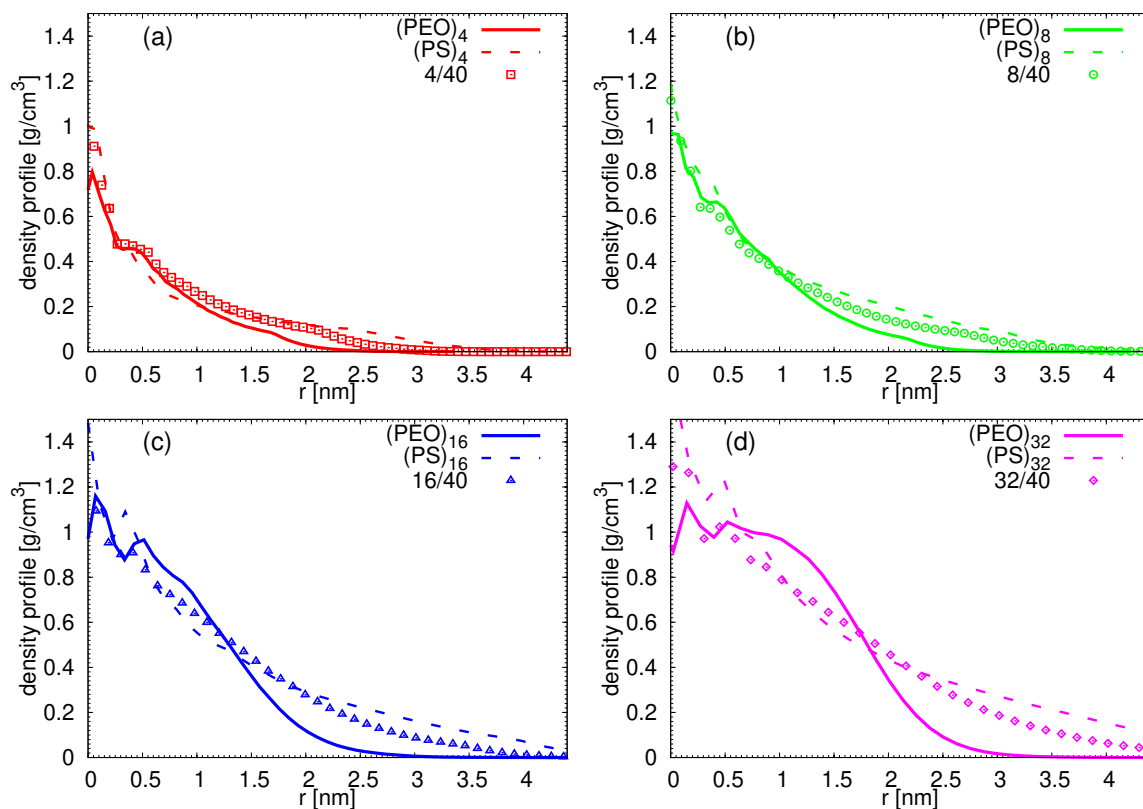
**Figure S1** (a) Illustration of the division of the PEO arm into 5 regions and of the segmental vectors for both star components. Regions are labeled from the core (black beads representing united atoms of PEO arm), i.e., from 1 (grey) to 5 (dark green) in the direction from the core to the end of the arm. (b,c) Examples of the fitting procedure of the correlation functions of the segmental vectors in 16/40 stars in the PB matrix (b) and in vacuum (c). Symbols represent the simulation data, the lines of the same color (also in agreement with (a)) are the corresponding fits.

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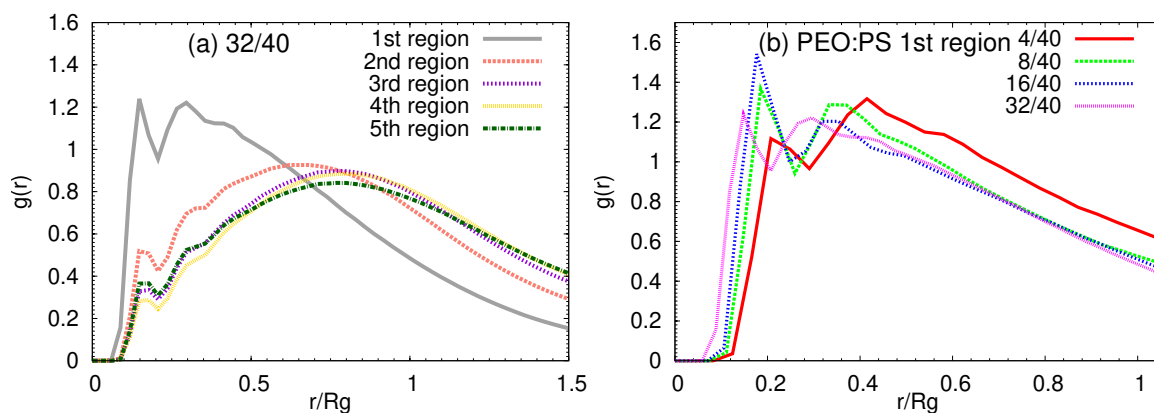
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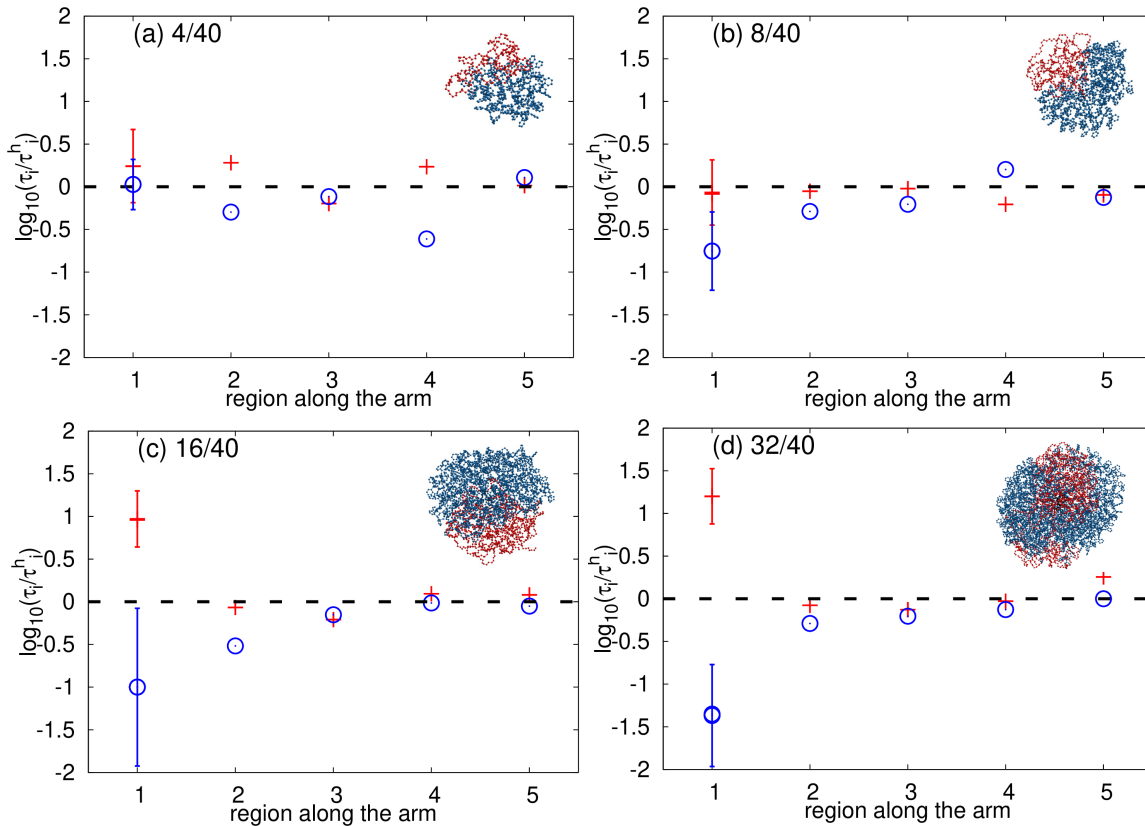
<sup>d</sup> Department of Mathematics and Applied Mathematics, University of Crete, GR-70013 Heraklion, Crete, Greece. Email: harman@uoc.gr



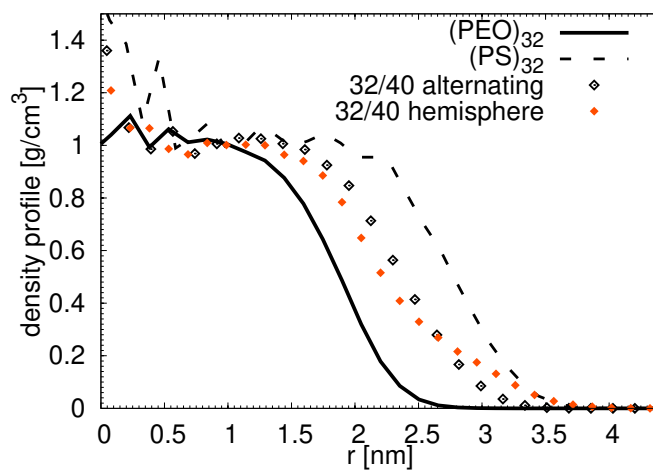
**Figure S2** Density profiles of the mikto-arm stars  $f/40$  in the PB matrix in comparison to their homopolymer analogues  $(\text{PEO})_f$  and  $(\text{PS})_f$ . (a) Stars with 4 arms, (b) 8 arms, (c) 16 arms and (d) 32 arms.



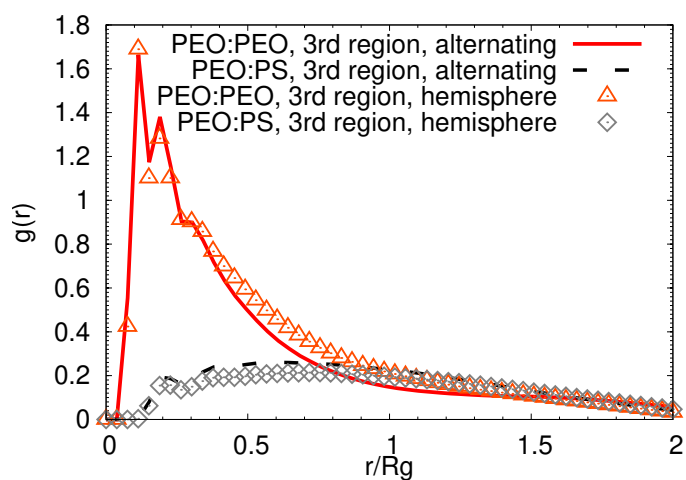
**Figure S3** Probability distribution of the PEO:PS distances in 5 regions along the arm for (a) 32/40 star in the PB matrix. (b) Probability distribution of the PEO:PS distances in the first region along the arm for all simulated stars in the PB matrix. Regions are labeled from the core, i.e., from 1 to 5 in the direction from the core to the end of the arm. The functions are normalized in a way that the integral under each curve equals to 1.



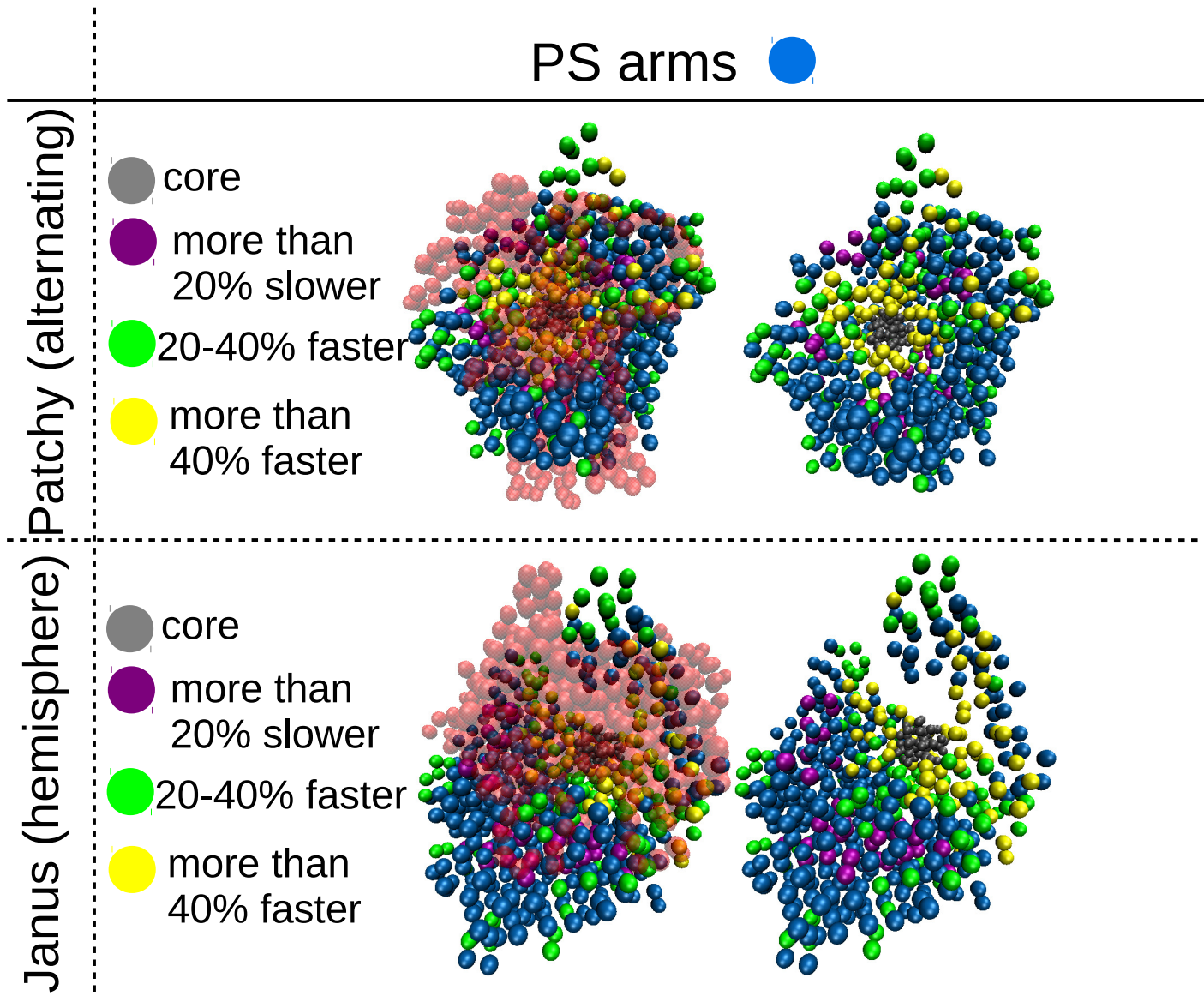
**Figure S4** Relaxation times of the segments placed in the regions along the arm normalized by the values of the relaxation times  $\tau_i^h$  of a corresponding regular homopolymer star for the systems in vacuum. Regions are labeled from the core, i.e., from 1 to 5 in the direction from the core to the end of the arm. The red crosses correspond to PEO arms and the blue stars to PS arms. The error bars were obtained by block averaging method and are of the same order or smaller in the remaining regions. The insets show randomly selected snapshots of the system with the corresponding coloring code.



**Figure S5** Density profiles of the mikto-arm stars 32/40 with alternating and hemisphere attachment in vacuum in comparison to their homopolymer analogues  $(\text{PEO})_{32}$  and  $(\text{PS})_{32}$  in the same environment.



**Figure S6** Comparison of the distribution functions of the PS:PEO and PEO:PEO monomer pair distances in the third region of 32/40 stars with either Janus (hemisphere attachment, symbols) or patchy morphology (alternating attachment, lines). The functions are normalized in a way that the integral under the sum of the curves (PS:PEO and PEO:PEO pairs) equals to 1.



**Figure S7** Spatial representation of the slow and fast domains consisting of PS monomers (beads) in the 32/40 mikto-arm stars. The relative acceleration or slowing down of the dynamics is obtained by comparing the average displacements at  $t = 1$  ns of the monomers of the 32/40 stars, with respect to the corresponding monomers of the homopolymer star analogues. The left snapshots include also transparent monomers of the complementary component. For a better visualization, we chose a monomer radius much smaller than the one which would correspond to each chemical unit and therefore the monomers may look like they are not connected.