Electronic Supplementary Information for:

Influence of wall heterogeneity on nanoscopically confined polymers

Raffaele Pastore,[*,†,‡,¶] Alessio David,[¶] Mosè Casalegno,[¶] Francesco Greco,[†] and Guido Raos[*,¶]

† *Department of Chemical, Materials and Production Engineering, University of Naples Federico II, P. le Tecchio 80, Napoli 80125, Italy*

‡ *CNR-SPIN, Via Cintia, 80126 Napoli, Italy*

¶ *Dipartimento di Chimica, Materiali e Ingegneria Chimica G. Natta, Politecnico di Milano, via L. Mancinelli 7, 20131 Milano, Italy*

E-mail: raffaele.pastore@unina.it; guido.raos@polimi.it

Horizontal and vertical components of the EEVA - Fig.ESI1 shows the EEVA components along the unconfined/horizontal directions and the confined/vertical one, $X_{xy} = \frac{X_x(t) + X_y(t)}{2}$ and $X_z(t)$, for $\alpha = \pm 1$. The figure clarifies that the effect of the vertical confinement does not lead to a marked spread of the relaxation dynamics along the different directions, as the two components behave similarly, especially at long time.

Long time decay of the EEVA - The EEVA relaxation in our systems is well fitted by a double exponential decay: at short time, $X(t) \simeq A_s e^{-t/\tau_s}$, while the late decay is well described by, $X(t) \simeq A_l e^{-t/\tau_l}$, with characteristic times $\tau_l \gg \tau_s$. It is worth noticing that double exponential decay can be considered as a "stronger" deviation from simple exponential, as compared to a stretched exponential. This is somehow expected in our
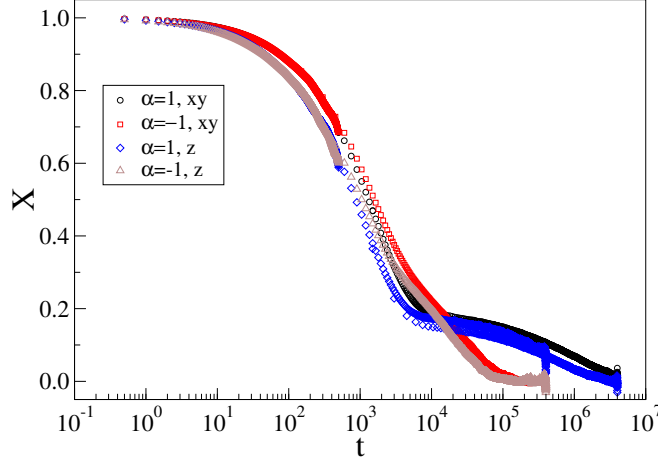
Figure ESI1: Horizontal and vertical EEVA components (xy and z, respectively, as indicated) as a function of time and for $\alpha = \pm 1$.

systems, because of the strong "polarization" of the chain ensemble in fast and slow chains. Stretched exponential decay is instead expected in the presence of a broad but continuous spectrum of relaxation times.

As mentioned in the main text, we use the late exponential to define the longest relaxation time, τ_l. Fig. ESI2 demonstrates the robustness of this fit, when t becomes comparable to τ_l or larger: after rescaling time and EEVA by the inverse fitting parameters, τ_l^{-1} and A_l^{-1}, respectively, data for all α values collapse on a single exponential master curve.
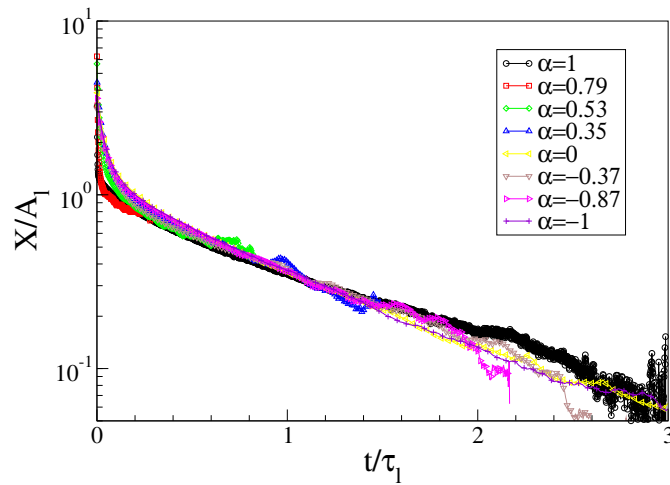

Figure ESI2: $X(t)/A_l$ versus t/τ_l for the different values of α. τ_l and A_l are obtained from an exponential fit to the late decay of EEVA, $X(t) = A_l e^{-t/\tau_l}$.

2

First and second layer for the $\alpha = -1$ system - Fig. ESI3 shows the configuration of the polymer beads within the first two thin layers, on top of an $\alpha = -1$ surface. As in the $\alpha = 1$ case, discussed in the main text, the density in the second layer appears to be smaller than in the first one. Such density oscillations are well known and they occur even on perfectly homogeneous case.[2] They persist for just two or three bead diameters, in the case of the short-FENE model adopted in our simulations.[1] As regards the structural changes in the horizontal plane, instead, the first layer show differences with respect to the $\alpha = 1$ case, with local order and density being homogeneous and, roughly speaking, intermediate between the two halves of the $\alpha = 1$ first layer. This is expected from the fact that such configurations are strongly sensitive to the wall morphology: finely and homogeneously intermixed ($\alpha = -1$) versus fully segregated W and S sites ($\alpha = 1$).
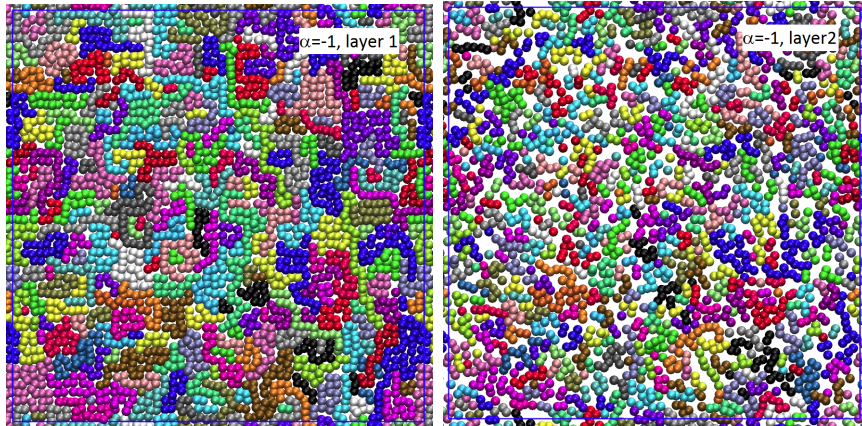

Figure ESI3: snapshots of the first polymer layer ($0.6 < z \leq 1.4$) and the second polymer layer ($1.4 < z \leq 2.2$), on the $\alpha = -1$ surface. Polymer beads belonging to the same chain are represented with the same color.

Pair distribution functions - We have computed the pair distribution functions, $g_{2D}(r)$, among all the beads belonging to the first layer. Fig. ESI4 shows that $g_{2D}(r)$ for the $\alpha = \pm 1$ systems are remarkably similar, except for some minor feature around $r = 1.4$ that cannot be easily interpreted. An analogous in-plane structure factor, $S_{2D}(k)$, should display significant features at wave vectors k corresponding to the length scale of the heterogeneities on the underlying surface. Alternatively, more sophisticated and higher order spatial correla-
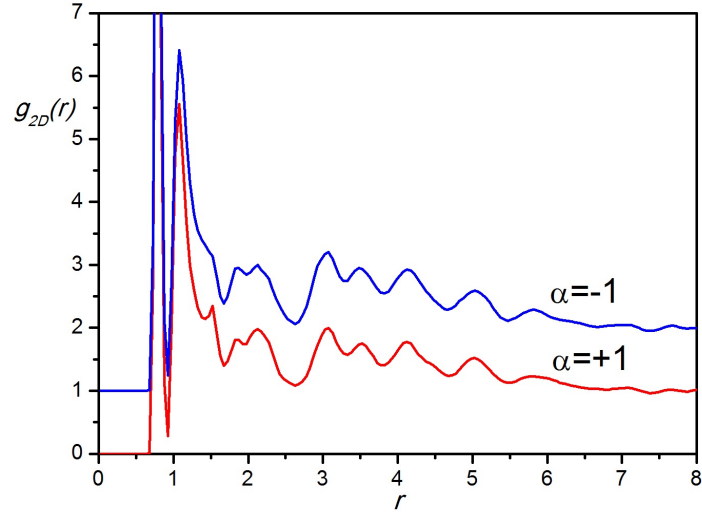
Figure ESI4: Pair distribution functions within the first polymer layers ($0.6 < z \leq 1.4$), on the $\alpha = \pm 1$ surfaces.

tion functions may be useful to identify different structural features triggered by the different wall morphologies. For example, we expect that correlation functions focusing on the local order or on the local configurational entropy[3] may provide a correlation length that varies alike to typical size of the surface chemical heterogeneity.

References

(1) Mackura, M. E.; Simmons, D. S. J. Polym. Sci. B: Polym. Phys. 52, 134 (2014).

(2) Yethiraj, A. Advances in Chemical Physics 121, 89 (2002).

(3) Tanaka, H., et al., Nature Materials 9, 324 (2010).