Supplementary information: Polymer spreading on substrates with nanoscale grooves using molecular dynamics

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Potential function interactions. Figure S1 (a) and (b) depict the potential function interactions for Zdol and Z molecules, respectively. The potentials are identified using arrows and numbers that correspond to the equations that describe the potentials. These potentials are similar to validated potentials and parameters used in previous research. A truncated, shifted Lennard Jones potential U_{LJ} exists between all polymer beads, given by

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} - \left(\frac{\sigma}{r_c}\right)^{12} + \left(\frac{\sigma}{r_c}\right)^{6}\right], \quad (1)$$

where r is the distance between two beads, σ = 0.7 nm is the bead diameter, r_c = 2.5 σ is the cutoff distance within which interactions between neighboring beads are considered, and $\varepsilon = Tk_B$ is the potential well depth, where T = 300 K is the absolute temperature and k_B is the Boltzmann constant. A finitely extensible nonlinear elastic (FENE) potential U_{FENE} acts as a spring to bond neighboring beads of the same molecular chain, *i.e.*,

$$U_{FENE}(l) = -\frac{1}{2}kR_0^2 \ln\left[1 - \left(\frac{l - l_0}{R_0}\right)^2\right], \quad (2)$$

where l is the bond length, l_0 = 1.3 σ is the equilibrium bond length, R_0 = 0.3 σ indicates the maximum extensible range, and k = 40 ε/σ^2 is the spring constant. The substrate interacts with the polymer molecules via a dispersive van der Waals interaction $U_{bb\text{-}wall}$, described as

$$U_{bb-wall}(z) = 2\varepsilon\left[\frac{1}{2}\left(\frac{\sigma}{z}\right)^{9} - \frac{3}{2}\left(\frac{\sigma}{z}\right)^{3}\right], \quad (3)$$

where z is the distance between a substrate bead and a polymer bead. We use a short-range exponential potential $U_{eb\text{-}eb}$ to model the attraction of functional end beads to each other,

$$U_{eb-eb}(r) = -2\varepsilon \exp\left(-\frac{r - r_c}{d}\right), \tag{4}$$

where r_c = 1.0 σ is the cutoff distance and d = 0.3 σ is the decay length. Additionally, a fraction of the substrate beads is functional. An attractive force exists between functional substrate and functional polymer beads, also modeled by a short-range exponential potential $U_{eb\text{-}wall}$,

$$U_{eb-wall}(z) = -2\varepsilon \exp\left(-\frac{z - z_c}{d}\right), \tag{5}$$

where z_c = 1.165 σ is the cutoff distance.

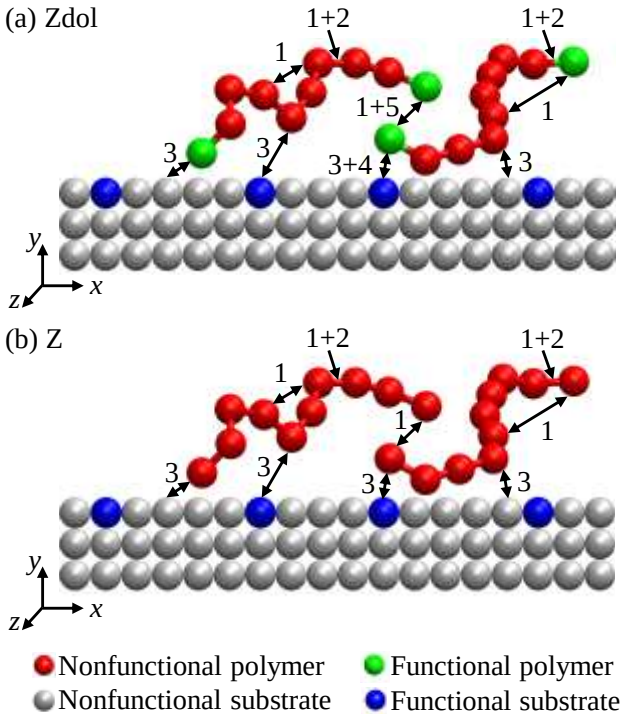

Figure S1. Schematic of potential function interactions for (a) Zdol and (b) Z polymer, with numbers referring to the corresponding equations.

Energy well example calculation. We use a triangular groove with θ = 120° as an example substrate to demonstrate how we quantify polymer clustering on the surface of substrates formed into grooves of different shapes. The minimum potential energy that occurs for this substrate E_{min} = -18.03ε is

located at the edge of the groove where the polymer beads cluster. We incrementally increase the potential energy while simultaneously quantifying the spatial region defined by the potential energy range, such that a region with low energy as opposed to a point with minimum energy is evaluated. Figure S2 shows the number of polymer beads located within the region defined by a particular potential energy range as a function of the potential energy range. We define the potential energy range E_{range} as the increase in potential energy from the minimum potential energy E_{min} that occurs for a particular substrate. The inset images show a 2D view of the polymer bead locations in the *x*-*y* plane at the end of the simulation. We only show the location where the potential energy is minimum so that clustering is discernable. Black dots represent the center of substrate beads, magenta dots represent the center of polymer beads located within the region described by the corresponding potential energy range, and grey dots represent the center of polymer beads located outside the region described by the corresponding potential energy range.

From Fig. S2 we observe that the number of polymer beads within the region described by the potential energy range increases with increasing potential energy range. We observe that this increase occurs slowly until, at $E_{range} = 4.2\varepsilon$, a sudden 78% increase occurs. Before this significant increase, we appear to converge on a single cluster of polymer beads at the edge of the groove, and after the 78% increase, multiple polymer bead clusters are found. Thus, we quantify the magnitude of the energy well created by the different groove shapes as the maximum potential energy range, measured from the minimum potential energy, that defines a spatial region in which the number of polymer beads does not increase by more than 20% with increasing potential energy. For this case, the energy well $E_{well} = 4.1\varepsilon$. The energy well quantifies the size of the polymer cluster at the edge of the groove and correlates to anisotropic spreading along the groove.

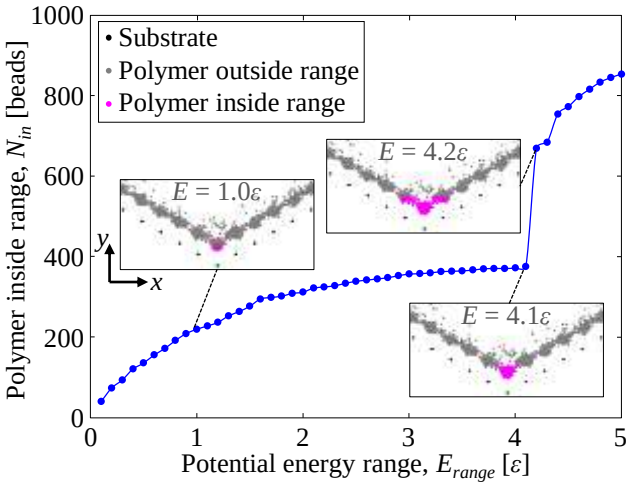

Figure S2. The number of polymer beads within the region described by the potential energy range at the end of the simulation as a function of the potential energy range for a triangular groove with $\theta = 120°$. Insets show a collapsed 2D view of the bead locations at the end of the simulation where magenta dots represent the center of polymer beads located within the corresponding potential energy range.