Monomer-nanoparticle pair distribution functions:

To provide additional perspective on the interphase structure, we report the separate A and B monomer-nanoparticle radial pair distribution functions in Figure S1. Note that this data contains the same information as Figure 3 from the main text, but here is represented in the more common form.

Figure S1: Monomer–nanoparticle radial pair distribution functions for the various copolymer and homopolymer systems, as labeled.
Chain orientations:
To further characterize chain conformations in the interphase, we measure chain orientations with respect to the nanoparticle using an orientation parameter based on the second-order Legendre polynomial.\([\text{?}]\) Specifically,

\[
\langle P_2(\cos \theta_{ee}) \rangle = \frac{3 \langle \cos^2 \theta_{ee} \rangle - 1}{2},
\]

where \(\theta_{ee}\) is the angle between the polymer end-to-end vector and the vector from the nanoparticle to the polymer’s center of mass. When the chain end-to-end vector tends to align parallel to the nanoparticle radial vector, \(\langle P_2(\cos \theta_{ee}) \rangle > 0\), while \(\langle P_2(\cos \theta_{ee}) \rangle < 0\) indicates a tendency to align parallel to the nanoparticle surface. \(\langle P_2(\cos \theta_{ee}) \rangle = 0\) is consistent with random orientation. Figure S2 reports \(\langle P_2(\cos \theta_{ee}) \rangle\) as a function of distance of the polymer’s center of mass from the nanoparticle center. Close to the nanoparticle, chains tend to orient parallel to the nanoparticle surface, although this effect is reduced in some of the blockier systems. At intermediate distances, between approximately 10\(\sigma\) and 15\(\sigma\), the block copolymer chains show a slight tendency to align parallel to the nanoparticle radial vector as the adsorbing end of the chain remains close to the nanoparticle and the non-adsorbing end remains farther away; this effect is minimal in the \(B_L = 1\) system and is not observed in the homopolymer systems.

Figure S2: Chain end-to-end orientation parameter, as defined in the text above, for the various copolymer and homopolymer systems, as labeled. Chains are assigned to concentric spherical shells around the nanoparticle based on their center of mass, and shells have width of 1\(\sigma\). Adequate statistics were not obtained to report on the rare cases where a polymer’s center of mass resides at \(r < 3.5\sigma\).
**Bond orientations:**

We can characterize bond orientations similarly to chain orientations by examining $\langle P_2(\cos \theta_{bv}) \rangle$, where $\theta_{bv}$ is the angle between the bond vector and the vector from the nanoparticle to the center of the bond. Figure S3 reports $\langle P_2(\cos \theta_{bv}) \rangle$ as a function of distance of the bond from the nanoparticle center.

![Graph](image)

Figure S3: Bond vector orientation parameter, as defined in the text above, for the various copolymer and homopolymer systems, as labeled. Bonds are assigned to concentric spherical shells around the nanoparticle based on the bond center, and shells have a width of $0.25\sigma$.

While there is relatively little variation between copolymer systems, the trend in bond orientations roughly mirrors the local monomer density (Figure 3a in the main text), with bonds in areas of higher relative monomer density being more likely to be orientated parallel to the nanoparticle surface and bonds in areas of lower relative monomer density being more likely to be oriented parallel to the nanoparticle radial vector.

The $B_L = 5$ system exhibits a higher peak at $6\sigma$ to $6.5\sigma$ compared to the other copolymer systems, likely because of the sharp microphase boundary (Figure 3b in the main text).

**References**