Supplementary Material

1. Asphericity of hydrophobic PCL core

Many studies have been put forth to measure the asphericity of a cluster or group.[1, 2] In this study, the asphericity of the hydrophobic PCL core was determined by employing a theoretical model that was established by Bruns and Carl as shown in Equation S1.[2]

$$\text{Asphericity} = 1 - 3\left\langle \frac{x^2y^2 + y^2z^2 + z^2x^2}{(x^2 + y^2 + z^2)^2} \right\rangle \qquad \text{(S1)}$$

where x, y and z are the principal moments. An asphericity value of 0 is achieved for a perfect sphere. The asphericity of the core causes a broadened distribution of the PCL and PEG blocks as well as water (Figure S1). This broadening results in a significant overlap between the radial density distribution curves, although the PEG blocks do not penetrate into the collapsed hydrophobic PCL core of the SCPs, i.e. the PCL core excludes not only the water, but also the PEG blocks. As shown in Figure S1, the density of PCL (N_{PCL} = 18) that is obtained from the MD simulations is similar to the bulk density reported for PCL (1.15 $g \cdot cm^{-3}$) of a similar MW.[3]

2. End-to-End distance and conformation of PEG

As shown in Figure S2, the EED_{PEGarm} of the PEG blocks of the SCPs investigated in this study increase with increasing MW_{PEG}. For SCPs with $N_{PEG} \leq 12$, the EED_{PEGarm} distribution of each PEG arm is similar within a given SCP. In contrast, the distribution of EED_{PEGarm} differs amongst arms for SCP with $N_{PEG} \geq 19$, for which PEG arm sampling remains unconverged within 200 ns (Figure S2). Nevertheless, the radius of gyration of PEG, averaged over all arms converges for all SCPs investigated in this study (Figure S3). For SCPs with $N_{PEG} > 12$, the distal ends of the PEG blocks often extend away from the center of the hydrophobic core, and then curl back providing protection of the hydrophobic core (see trajectory movie). Furthermore, hydrogen-bond "bridges" between PEG arms or PEG repeat units were observed as shown in Figure S4.

3. Theoretical model for predicting the structural properties of PEG

Previously, Flory put forth the "random flight" model to predict the size of linear polymers in terms of the radius of gyration, Rg (the average root mean square distance of a segment from the COM of the molecule).[4] Rg is approximately proportional to $R/\sqrt{6}$, where R, the root mean square end-to-end distance, scales with the size of the monomer, a, and the degree of polymerization of the polymer to a power law (i.e. $R \approx aN^{\alpha}$).[5] In a theta solvent, the polymer behaves ideally and exists as a Gaussian coil with an α value of 0.5. In a poor solvent, the polymer is closely packed and has an α value of ⅓.[5] In a good solvent, the radius (R) is known as the Flory radius with an α value of 0.588 ($R_F = aN^{\alpha}$).[5] In the current study, the size of the PEG chain can be expressed in terms of the Rg based on Flory's theory:

$$Rg_{FloryPEG} = \frac{a}{\sqrt{6}} N_{PEG}^{\ \alpha}, \quad \text{where a = 0.28 nm for PEG.}[6] \qquad \text{(S2)}$$

References

1. Ding, W. L., S.; Lin, J.; Zhang, L., *J. Phys. Chem. B.* **2008,** 112, 776-783.
2. Bruns, W.; Carl, W., *Macromolecules* **1991,** 24, 209-212.
3. Sigma-Aldrich, date of access: May 2009, http://www.sigmaaldrich.com..
4. Flory, P. J., *Principles of Polymer Chemistry, 1953, Cornell University Press, Ithaca, NY, Chapter 7.*
5. van der Maarel, J. R. C., *Introduction to Biopolymer Physics*. World Scientific Company: Singapore, 2007; Vol. Chapter 2.
6. Koenig, J. L.; Angood, A. C., *J Polymer Science Part A-2-Polymer Physics* **1970,** 8, 1787-1796.

Supplemental Figures

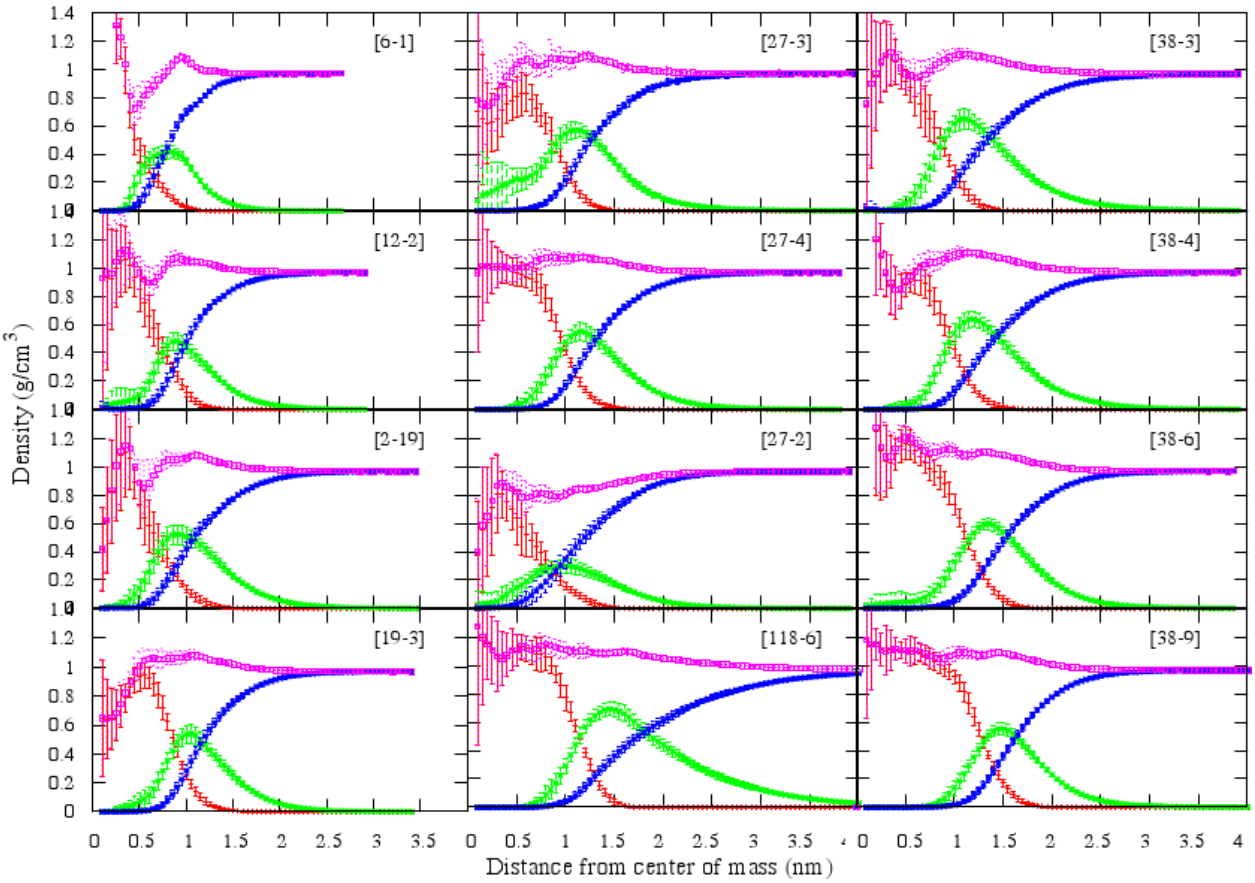

Figure S1: Density profiles of PEG (*), PCL (--), water (*) and the entire [MePEG$_x$-*b*-PCL$_y$]$_6$ star copolymer (□) as a function of distance from the center of mass of the hydrophobic core, averaged over the last 160 ns. The x and y values are labeled at the top right of the plots.

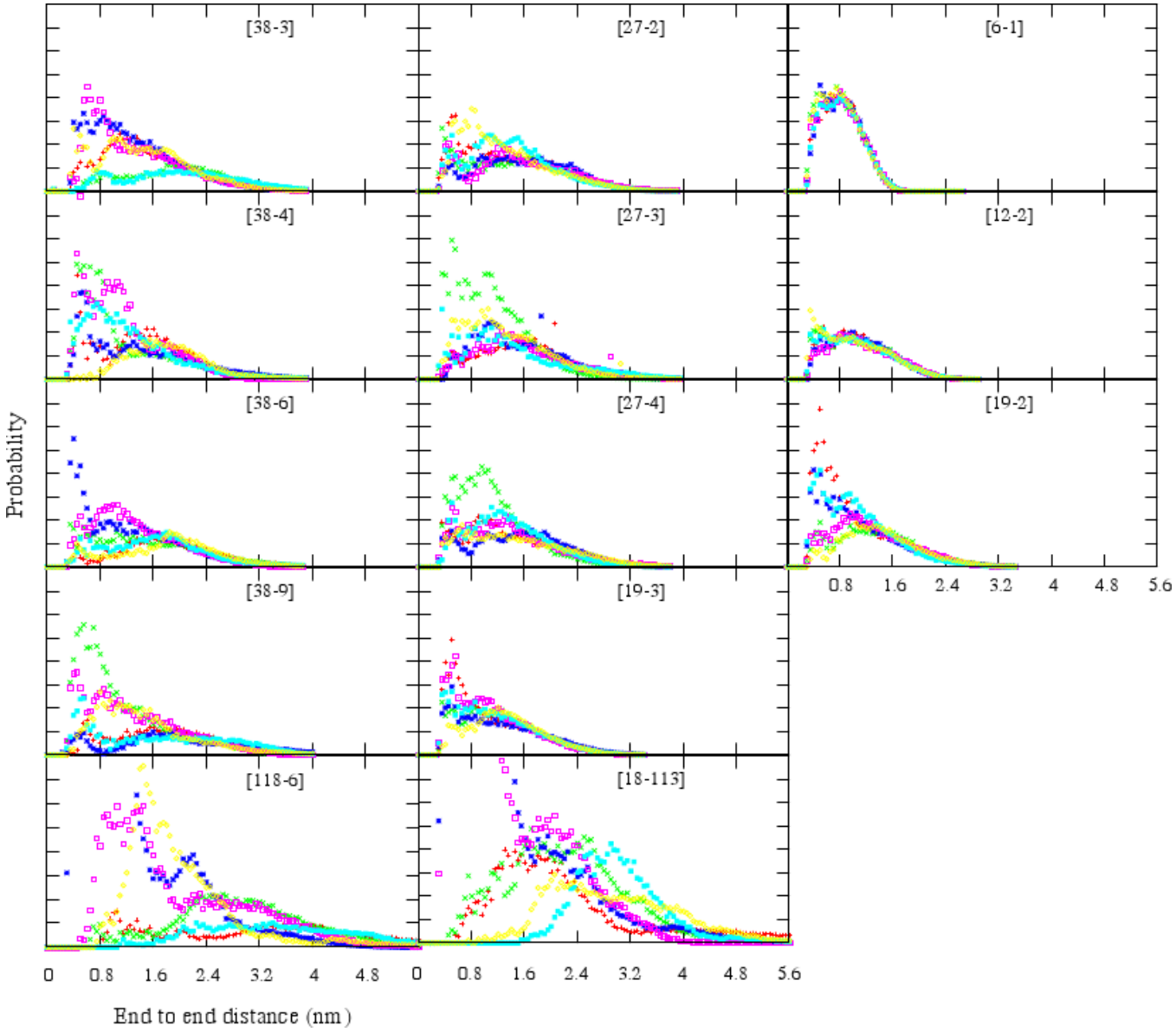

Figure S2: The distribution of the end-to-end distance of each of the PEG blocks of all $[MePEG_x\text{-}b\text{-}PCL_y]_6$ star copolymers, averaged over the last 160 ns of the molecular dynamics simulation. The x and y values are labeled at the top right of the plots.

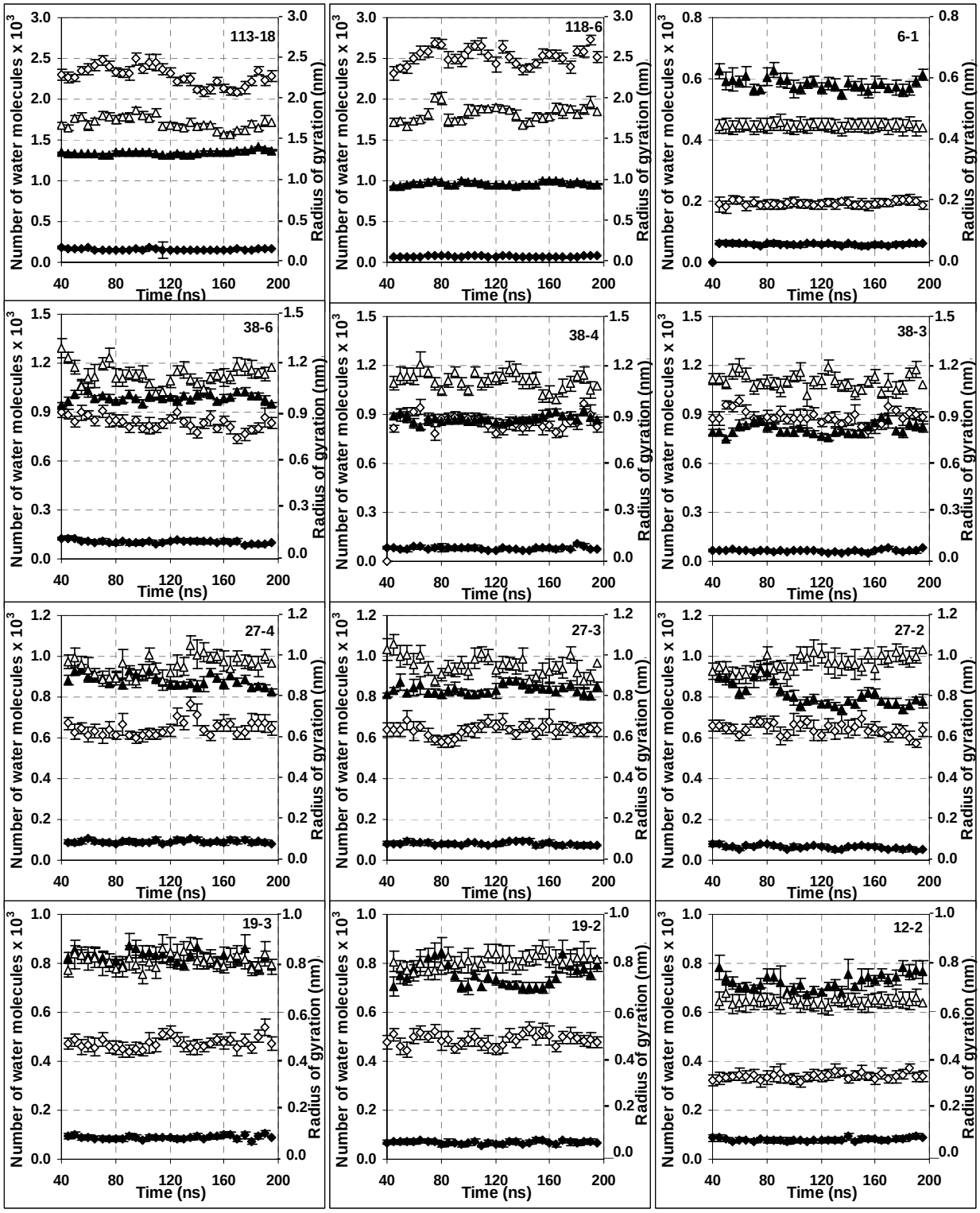

Figure S3: The hydration of PCL core (♦) and PEG blocks (◊) and the radius of gyration of PCL core (▲) and PEG blocks (□) of [MePEG$_x$-*b*-PCL$_y$]$_6$ star copolymer as a function of simulation time. The x and y values are labeled at the top right of the plots.

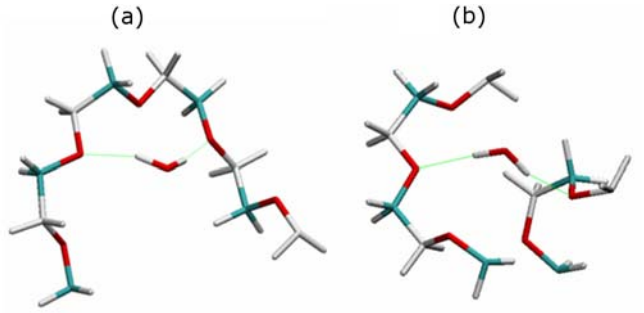

Figure S4: (a) Hydrogen bond (green line) formed between water molecule and the oxygen atoms of (**a**) PEG repeat units within the same PEG block or **(b)** "bridging" two PEG repeat units from different PEG blocks.