Supplemental Information for

Rod-Coil Block Copolymer Aggregates via Polymerization-Induced Self-Assembly

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CONTENT

1. The persistence length of rod blocks

The persistence length of rod block was calculated to evaluate the rigidity of rod blocks. The persistence length l_p is given by

$$\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \exp(-s / l_p) \qquad \text{(S-1)}$$

Here, $\mathbf{u}_i$ and $\mathbf{u}_j$ are the unit vectors of ith and jth bond, respectively. $s=|i\text{-}j|l_b$ is the contour distance between ith and jth bond, where l_b is the bond length. Here, l_b nearly equals to the equilibrium bond distance (*ca.* 0.8 r_c). In the simulation, we subjected a single rigid chain (k_θ =10) with 25 DPD beads in a simulation box of $L = 40r_c$ with periodic boundary conditions and full of solvent beads. The system was simulated with all a_{ij} equal to 25 for 2.0×10^6 DPD steps.

Figure S1 shows the plot of $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle$ as a function of s. By fitting the data with the Eq. S-1, we obtained the persistence length. The persistence length of rod blocks is *ca.* 20.7 r_c. Considering that the maximum targeted DP of rod blocks studied in this work is 10, the maximum contour distance s is *ca.* 7.2 r_c. The persistence length of rod blocks is significantly larger than the contour distance, indicating the sufficient rigidity of the rod blocks.
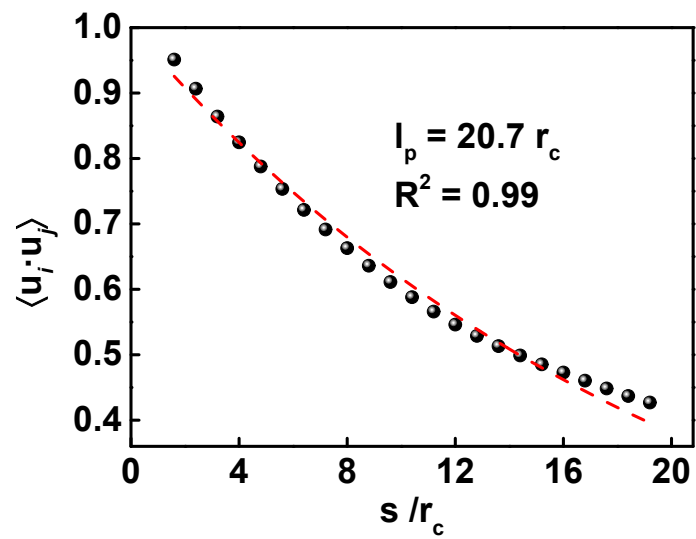
Figure S1. The plot of $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle$ as a function of s. The red dashed line is the fitting line.

2. Relationship between $k[C^*]$ and [M]

We calculated pseudo-first-order reaction rate constant $k[C^*]$ at different monomer concentrations [M] to figure out whether or not the $k[C^*]$ depends upon the concentration of monomers in the PISA. The results are shown in Figure S2. As shown, $k[C^*]$ depends significantly on [M]. However, $k[C^*]$ is unchanged at lower and higher [M], which correspond to the two linear regions in Figure 2. The lower and higher [M] correspond to the aggregate-dominated and free-chain dominated states, respectively. $k[C^*]$ decreases with the decrease of [M] in the range from [M]=1.5% to [M]=3.6% because of the heterogeneous growths of the free chain and the aggregated chain. As such, $k[C^*]$ is mainly governed by the state of copolymer chains (free chains and aggregated chains) rather than the concentration of monomers during the PISA.
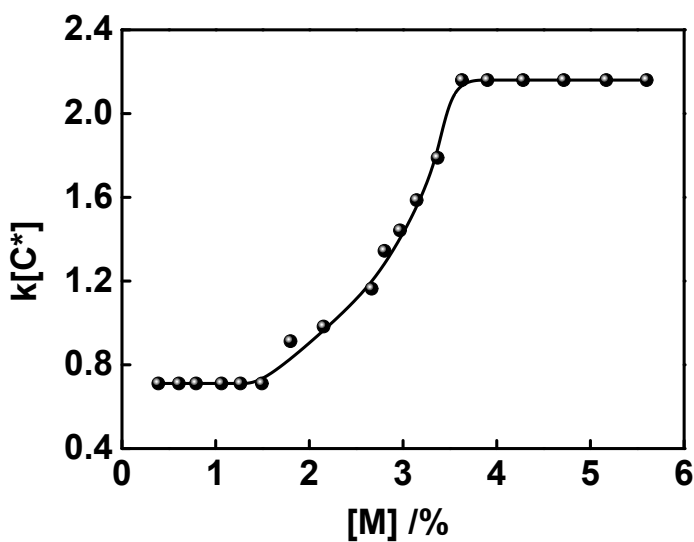
Figure S2. Plots of $k[C^*]$ as a function of monomer concentrations [M] during the PISA. The targeted DP of the rod blocks, the macromolecular initiator, and the copolymer concentrations are 7, C_3^*, and 8%, respectively.

3. Relationship between k and [C*]

Figure S3 shows the rate coefficient k against the initiator concentrations [C*]. The k values for the first linear (free-chain dominated) regions and the second linear (aggregated dominated) region are respectively given in the Figure. The values of k in the first linear region are almost unchanged with the increasing of [C*], denoting that k is independent of [C*]. This fact indicates that the polymerization in the first linear (free-chain dominated) region is similar to the free radical polymerization. In the second linear region, k increases with the increase of [C*]. In this region, the growth of the chains is limited by the aggregate. At higher [C*] (hydrophobic chain), smaller aggregates are formed, and therefore, the chains are less confined and can grow more rapidly.
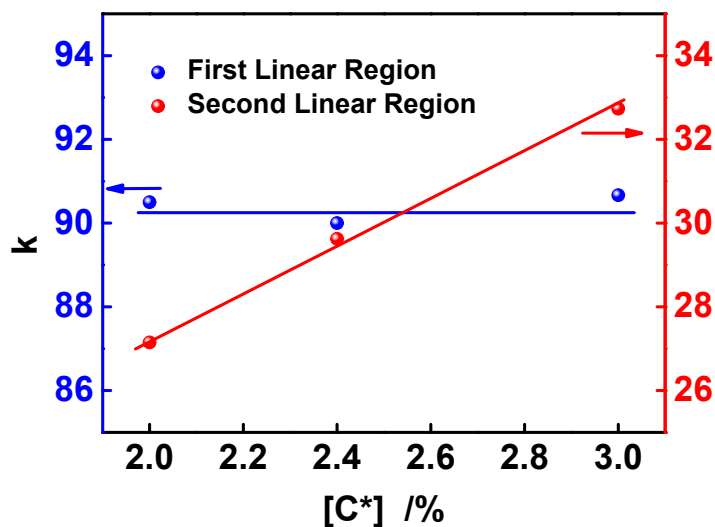
Figure S3. Plots of the rate coefficient k against initiator concentrations [C*] in the first and second linear regions. The macromolecular initiator and the copolymer concentrations are C_3* and 8%, respectively.