**Supporting Information**

**Impact of Copolymer Architecture on Demicellization and Cargo Release via Head-to-Tail Depolymerization of hydrophobic moieties.**

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**Table 1S.** The number of encapsulated cargo molecules in micelles formed from mixtures containing 1000 linear or miktoarm copolymer chains with 2000 or 4000 cargo molecules C3. The different interaction parameters between hydrophobic C-C and B-C beads correspond to *T*\*=1.8,1.6, and 1.4. [*Φ*]=0.12.

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| --- | --- | --- | --- |
|  | Total C3 | encapsulated C3 | Ratio |
| A30B30, *T\**B *=* 1.8*T\**C *=* 1.8, *T\**B-C *=* 1.8 | 2000 | 816 | 0.408 |
| A30B30, *T\**B *=* 1.8*T\** C *=* 1.6, *T\** B-C *=* 1.8 | 2000 | 841 | 0.421 |
| A30B30, *T\**B *=* 1.8*T\** C *=* 1.5, *T\** B-C *=* 1.8 | 2000 | 860 | 0.430 |
| A30B30, *T\**B *=* 1.8*T\** C *=* 1.4, *T\** B-C *=* 1.8 | 2000 | 863 | 0.432 |
| A30B30, *T\**B *=* 1.8*T\** C *=* 1.4, *T\** B-C *=* 1.4 | 2000 | 1662 | 0.831 |
| A30(B15)2, *T\**B *=* 1.8*T\** C *=* 1.4, *T\** B-C *=* 1.4 | 2000 | 1651 | 0.826 |
| A30(B10)3, *T\**B *=* 1.8*T\** C *=* 1.4, *T\** B-C *=* 1.4 | 2000 | 1625 | 0.812 |
| A30B30, *T\**B *=* 1.8*T\** C *=* 1.4, *T\** B-C *=* 1.4 | 4000 | 3284 | 0.821 |

**Table 2S.** The preferential aggregation number (*N*p), the mean squared radius and gyration (<*Rg2*>), and the shape asymmetry parameter (*κ*2) of micelles formed by A30B30, A30(B15)2 and A30(B10)3 copolymers, and from their mixtures with 2000 C3 cargo molecules.

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| --- | --- | --- | --- |
|  |  |  |  |
|  | *N*p | <*R*g2> | *κ*2 |
| A30B30  | 44 | 115.5 ± 0.2 | 0.0162 ± 0.0009 |
| A30B30 + C3 | 51 | 126.8 ± 0.3 | 0.0126 ± 0.0006 |
| A30(B15)2  | 30 | 91.4 ± 0.2 | 0.031 ± 0.001 |
| A30(B15)2 + C3 | 39 | 108.4 ± 0.2 | 0.025 ± 0.001 |
| A30(B10)3 | 23 | 82.1 ± 0.3 | 0.049 ± 0.002 |
| A30(B10)3 + C3 | 31 | 97.9 ± 0.4 | 0.041 ± 0.002 |

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**Figure 1S** Depolymerization fraction of end cap beads of A30B30,A30(B15)2, and A30(B10)3 copolymers as a function of time for constant trigger molecules concentration. RPT=10-2, RPB=10-3. [*ec*]0 is the initial end cap beads concentration, [*ec*]t is the end cap concentration.

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**Figure 2S** Depolymerization fraction of end cap (ec) beads of A30B30,A30(B15)2, and A30(B10)3 copolymers as a function of time for 10 times the stoichiometric trigger molecules concentration. RPT=10-4, RPB=10-3. [*ec*]0 is the initial end cap beads concentration, [*ec*]t is the end cap concentration.

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**Figure 3S** Mass distribution of micelles formed by linear A30B30 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=9100τ, 0.17, c) *t*=13500τ, 0.32, d) *t*=18000τ, 0.44, e) *t*= 27000τ, 0.61, f) *t*= 36500τ, 0.74. The trigger molecule concentration is maintained constant in all cases. RPT=RPB=10-3.

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**Figure 4S** Mass distribution of micelles formed by miktoarm A30(B15)2 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=4500τ, 0.10, c) *t*=9000τ, 0.24, d) *t*=18000τ, 0.45, e) *t*= 27000τ, 0.59, f) *t*= 45000τ, 0.76. The trigger molecule concentration is maintained constant in all cases. RPT= RPB=10-3.

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**Figure 5S** Mass distribution of micelles formed by miktoarm A30(B10)3 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=4500τ, 0.11, c) *t*=13500τ, 0.34, d) *t*=22500τ, 0.49, e) *t*= 36000τ, 0.63, f) *t*= 63000τ, 0.76. The trigger molecule concentration is maintained constant in all cases. RPT=RPB=10-3

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**Figure 6S** Mass distribution of micelles formed by linear A30B30 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=4500τ, 0.27, c) *t*=6000τ, 0.41, d) *t*=7500τ, 0.55, e) *t*= 9000τ, 0.68, f) *t*= 10500τ, 0.80. The trigger molecule concentration is maintained constant in all cases. RPT=10-2 and RPB=10-3.

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**Figure 7S** Mass distribution of micelles formed by miktoarm A30(B15)2 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=3000τ, 0.30, c) *t*=4000τ, 0.45, d) *t*=6000τ, 0.67, e) *t*= 7500τ, 0.78, f) *t*= 9000τ, 0.86. The trigger molecule concentration is maintained constant in all cases. RPT=10-2 and RPB=10-3.

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**Figure 8S** Mass distribution of micelles formed by miktoarm A30(B10)3 copolymers across various time points and depolymerization fractions of all hydrophobic beads: a) *t*=0, 0, b) *t*=3000τ, 0.37, c) *t*=4500τ, 0.56, d) *t*=6000τ, 0.68, e) *t*= 7500τ, 0.74, f) *t*= 9000τ, 0.80. The trigger molecule concentration is maintained constant in all cases. RPT=10-2 and RPB=10-3.

**a**

**b**

**Figure 9S** Cargo molecules release fraction from A30B30,A30(B15)2, and A30(B10)3 copolymer mixtures plotted against time for constant trigger molecule concentration. a) RPT=10-2, RPB=10-3 and b) RPT=10-3 and RPB=10-3. [*C*3]0 is the initial cargo molecules concentration, [*C*3]t is the cargo molecules concentration.

 **a**

**b**

**c**

**Figure 10S** Logarithmic plot depicting the fraction of released cargo molecules against time for a) linear A30B30,b) miktoarm A30(B15)2, and c) miktoarm A30(B10)3 copolymers. Fitting lines, *k* and *n* correspond to the Korsmeyer-Peppas equation. Trigger molecule concentration is maintained stoichiometric to end cap beads in all cases. RPT=10-4 and RPB=10-3.