**Supporting Information**

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

**Christos Gioldasis1, Apostolos Gkamas1 and Costas Vlahos1\***

1 Chemistry Department, University of Ioannina, 45110 Ioannina, Greece

**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.

|  |  |  |  |
| --- | --- | --- | --- |
|  | 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.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
|  | *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 |

**A graph of a function

Description automatically generated**

**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.

**A graph of a function

Description automatically generated**

**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.

**A group of graphs showing different colors

Description automatically generated with medium confidence**

**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.

**A group of graphs with different colored lines

Description automatically generated**

**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.

**A group of graphs with different colored lines

Description automatically generated**

**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

**A group of graphs with numbers

Description automatically generated with medium confidence**

**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.

**A group of graphs with different colored lines

Description automatically generated**

**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.

**A group of graphs with different colored lines

Description automatically generated**

**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 graph of a graph of a number of objects

Description automatically generated with medium confidencea**

**A graph of a graph showing a number of different colored lines

Description automatically generated with medium confidenceb**

**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 graph with a red line

Description automatically generateda**

**A graph with a red line

Description automatically generatedb**

**A graph with a red line

Description automatically generatedc**

**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.