

Thermoresponsive Block Copolymer Micelles with Tunable Pyrrolidone-based Polymer Cores Structure/Property Correlations and Their Application as Drug Carriers

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Supplementary Information

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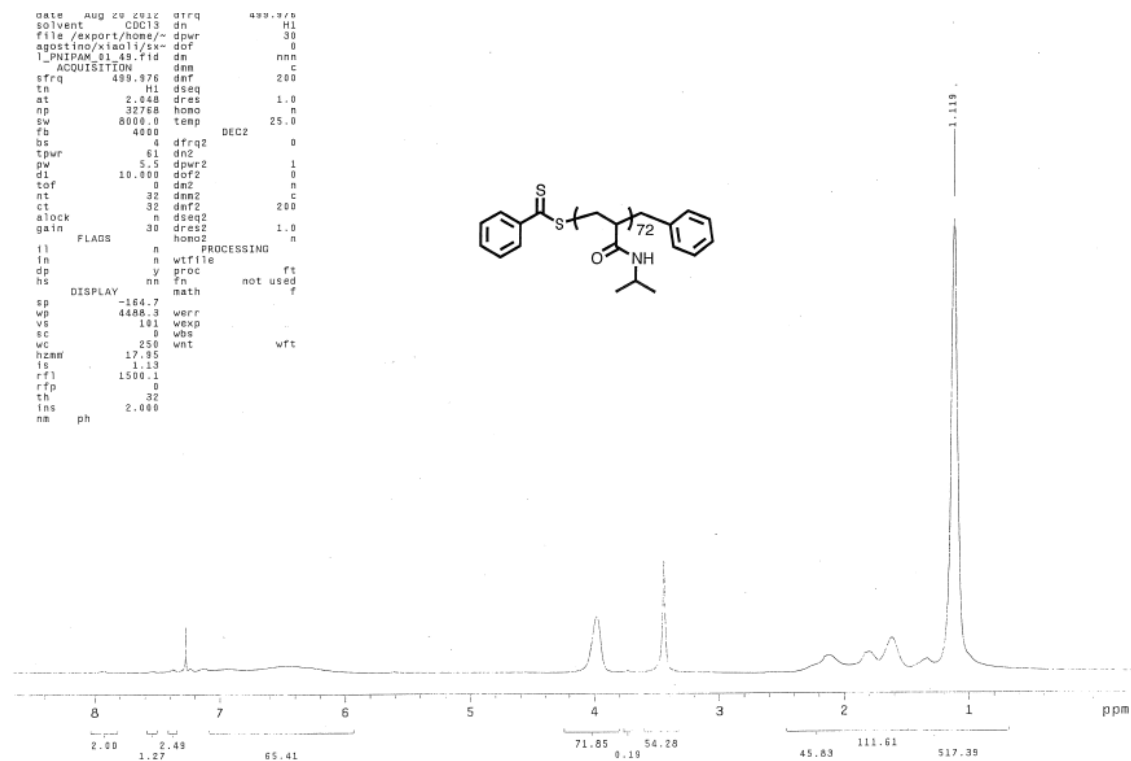


Figure S 1. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm-CTA.

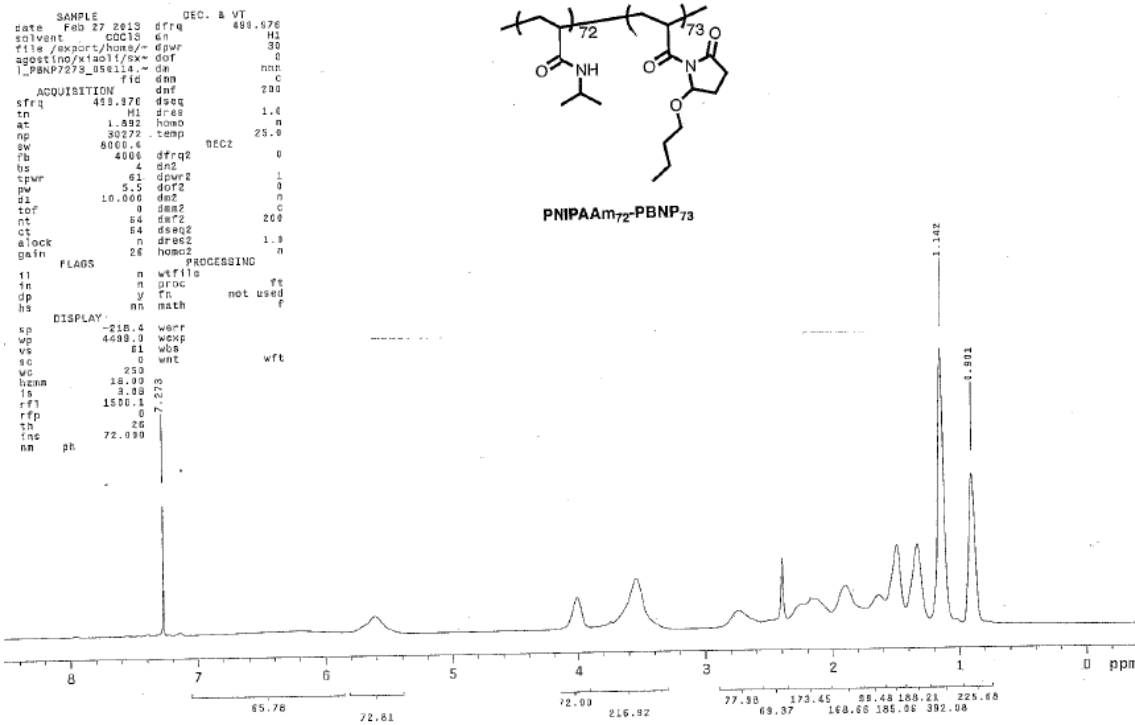


Figure S 2. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PBNP₇₃.

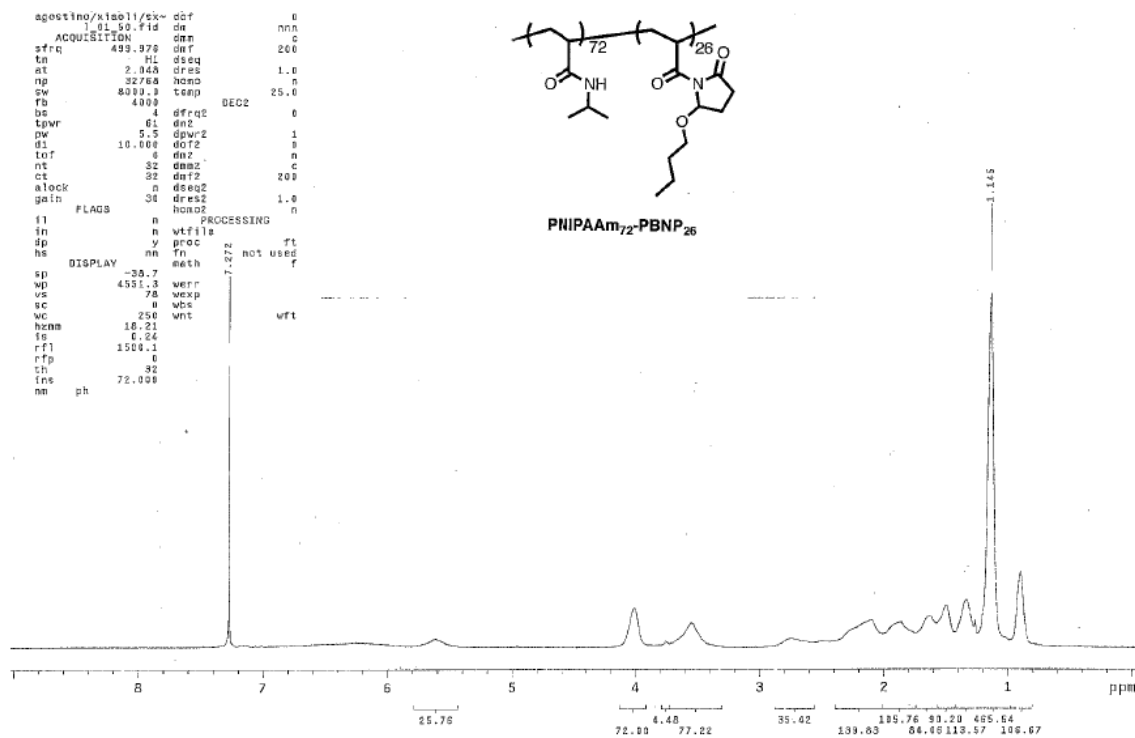


Figure S 3. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PBNP₂₆.

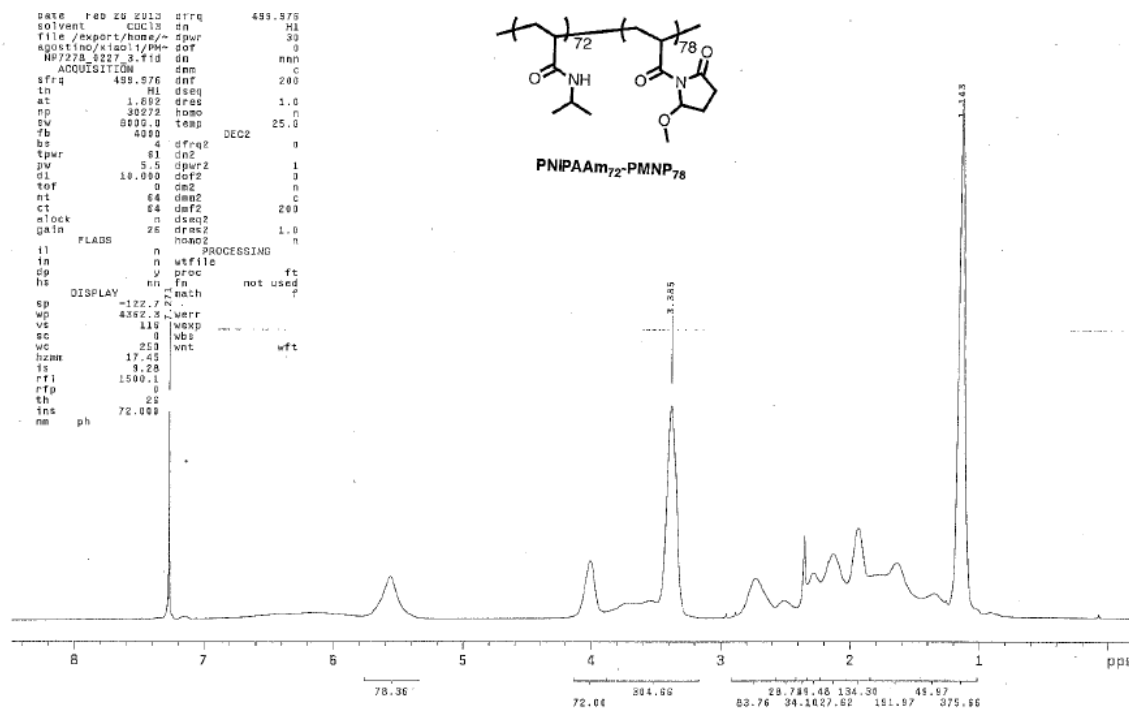


Figure S 4. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PMNP₇₈.

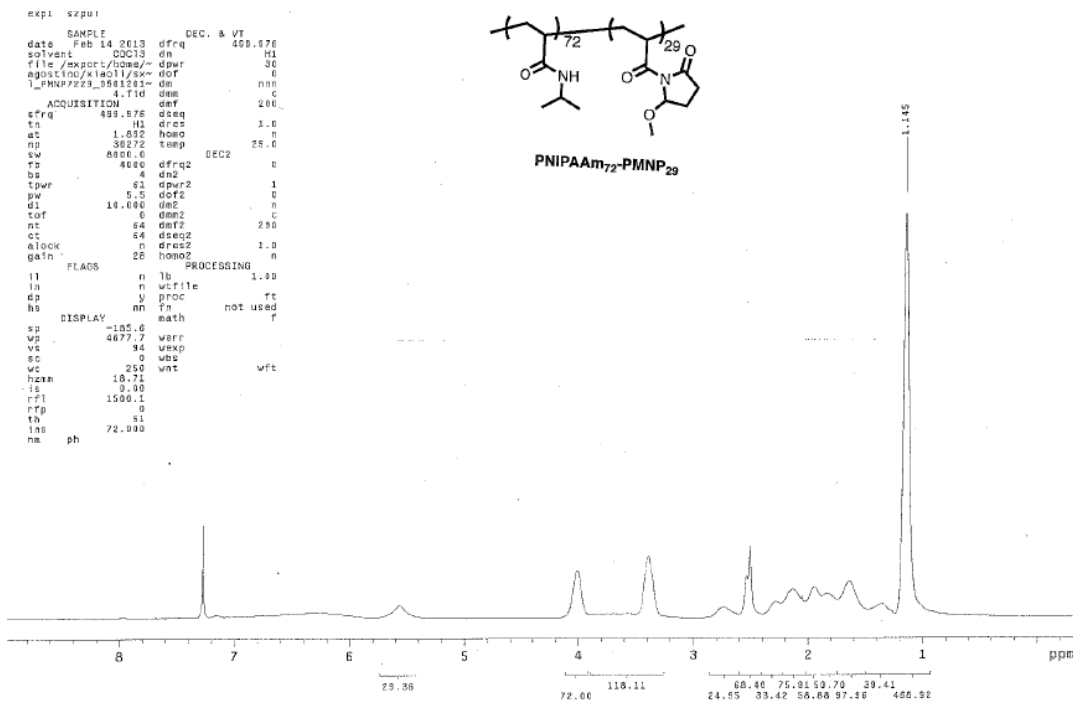


Figure S 5. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PMNP₂₉.

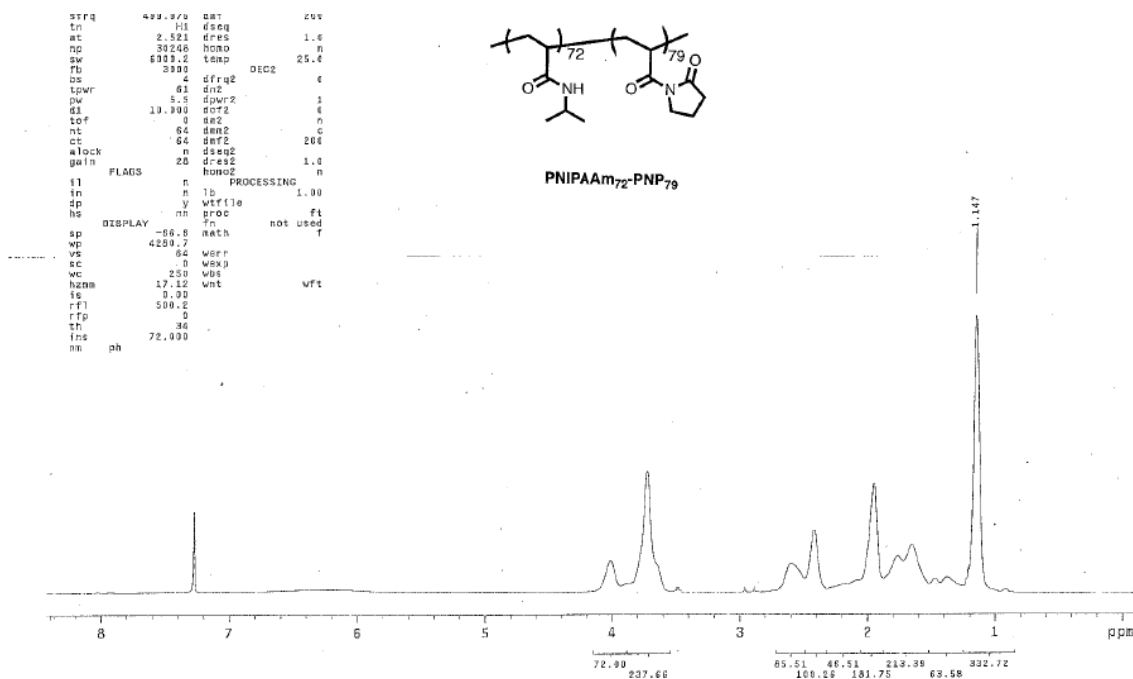


Figure S 6. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PNP₇₉.

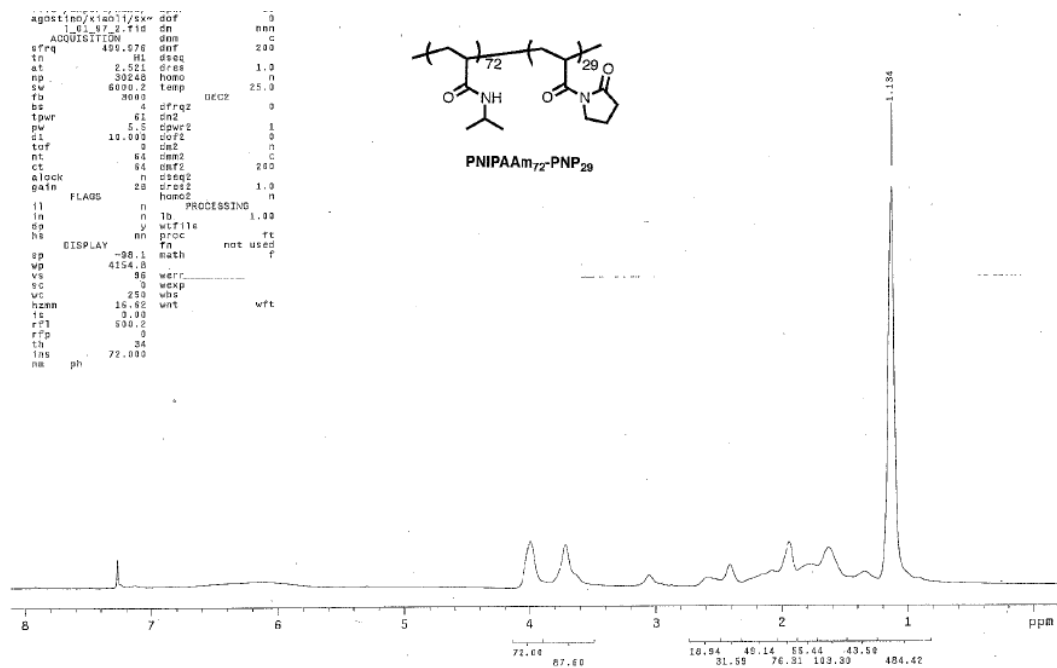


Figure S 7. ¹H NMR spectrum of (500 MHz, CDCl₃, 25 °C) of PNIPAAm₇₂-PNP₂₉.

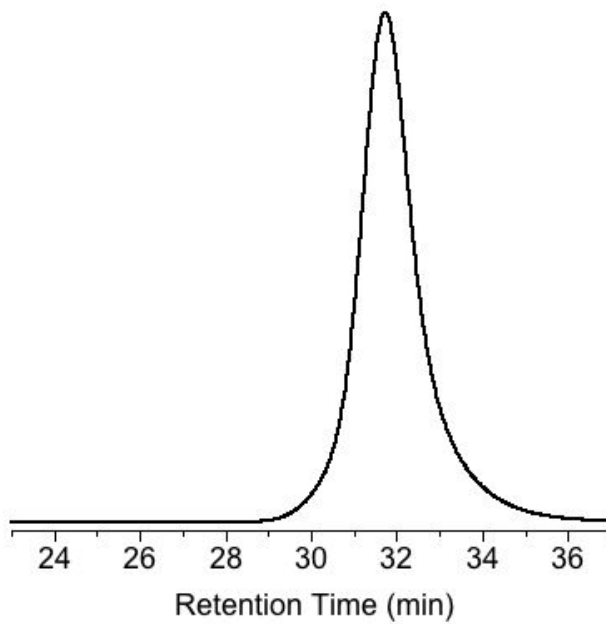


Figure S 8. GPC trace of PNIPAAm₇₂.

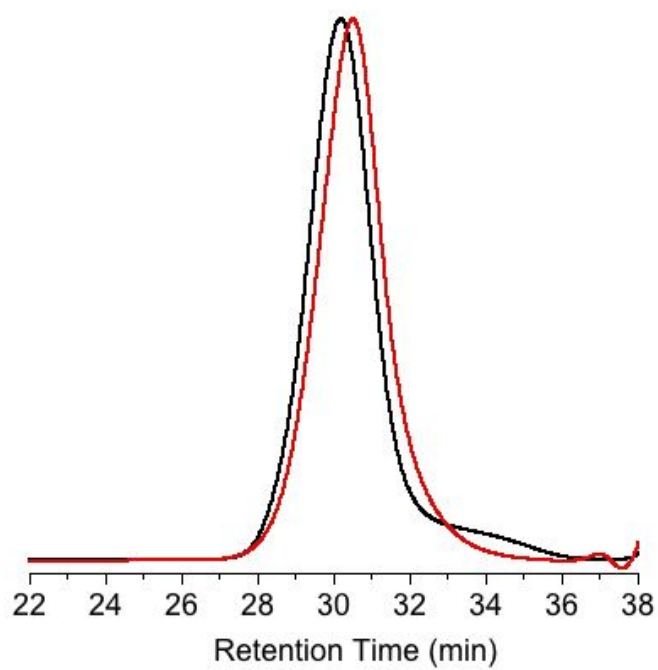


Figure S 9. GPC trace of PNIPAAm₇₂-PBNP₇₃ (black) and PNIPAAm₇₂-PBNP₂₆ (red).

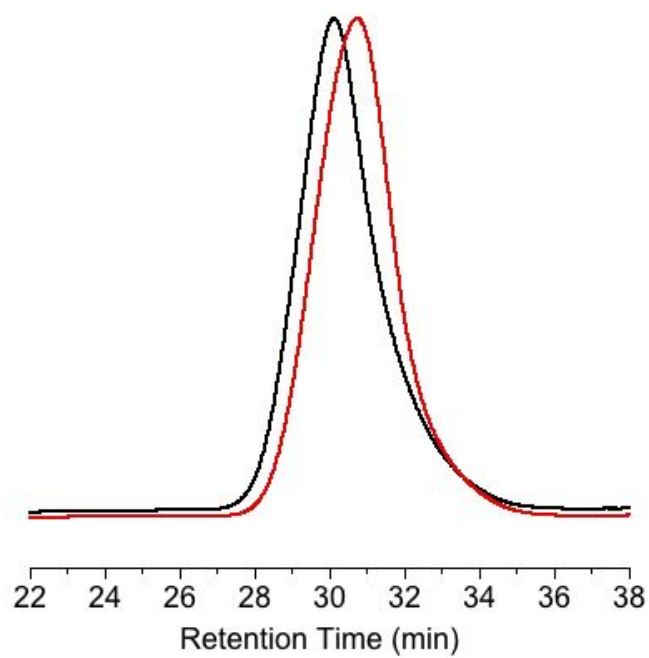


Figure S 10. GPC trace of PNIPAAm₇₂-PMNP₇₈ (black) and PNIPAAm₇₂-PBNP₂₉ (red).

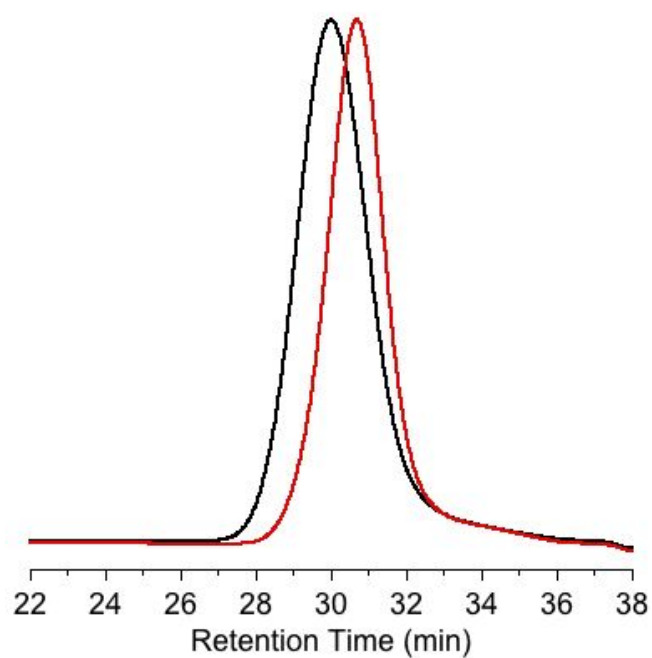


Figure S 11. GPC trace of PNIPAAm₇₂-PNP₇₉ (black) and PNIPAAm₇₂-PNP₂₉ (red).

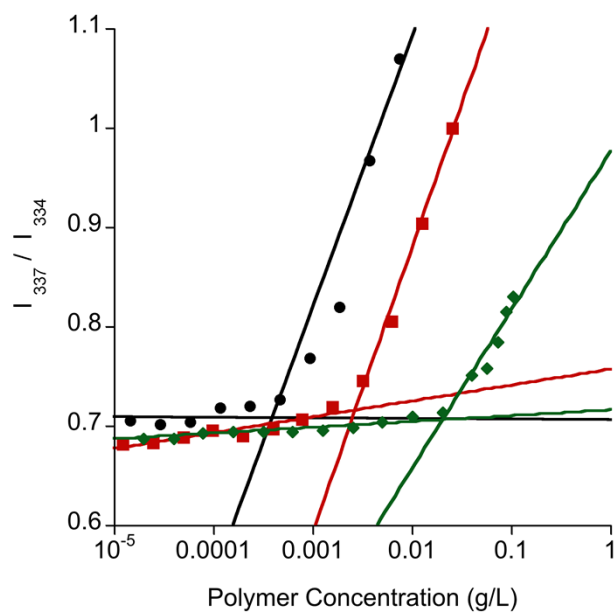


Figure S 12. The intensity ratio I_{337}/I_{334} obtained from pyrene excitation spectra of block copolymer solutions vs block copolymer concentration. PNIPAAm₇₂-PNP₇₉ (◊), PNIPAAm₇₂-PMNP₇₈ (◻), and PNIPAAm₇₂-PBNP₇₃ (●).

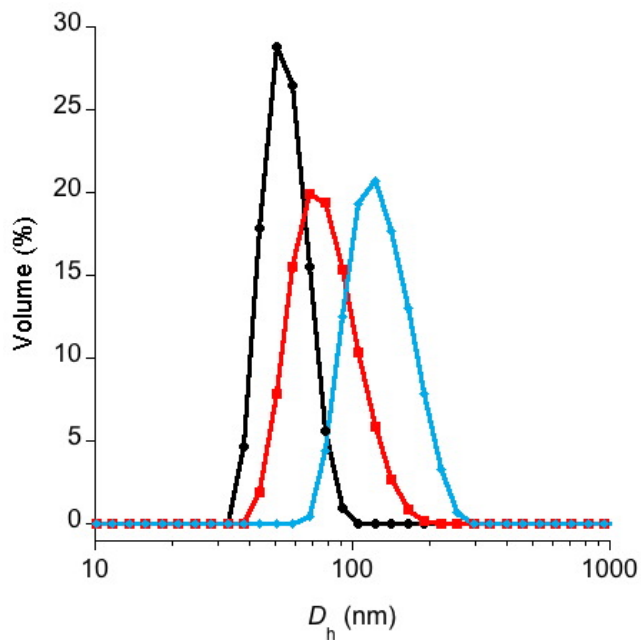


Figure S 13. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₂₆ (●), PNIPAAm₇₂-PMNP₂₉ (○), and PNIPAAm₇₂-PNP₂₉ (◆) micelles in water at 25 °C.

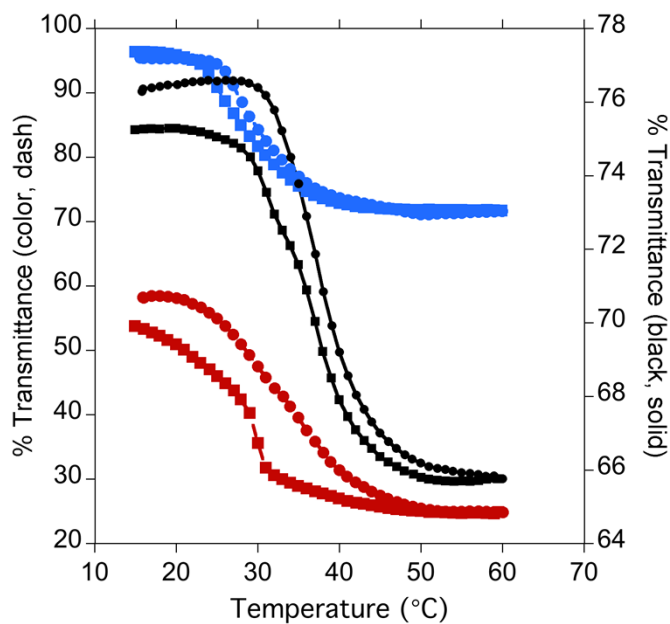


Figure S 14. Percentage transmittance versus temperature plot of PNIPAAm₇₂-PNP₇₉ (blue circle, dash, forward scan, blue square, dash, reverse scan), PNIPAAm₇₂-PMNP₇₈ (red circle, dash, forward scan, red square dash, reverse scan), and PNIPAAm₇₂-PBNP₇₃ (black circle, solid, forward scan, black square, solid, reverse scan). (0.2 mg/mL, DI Water).

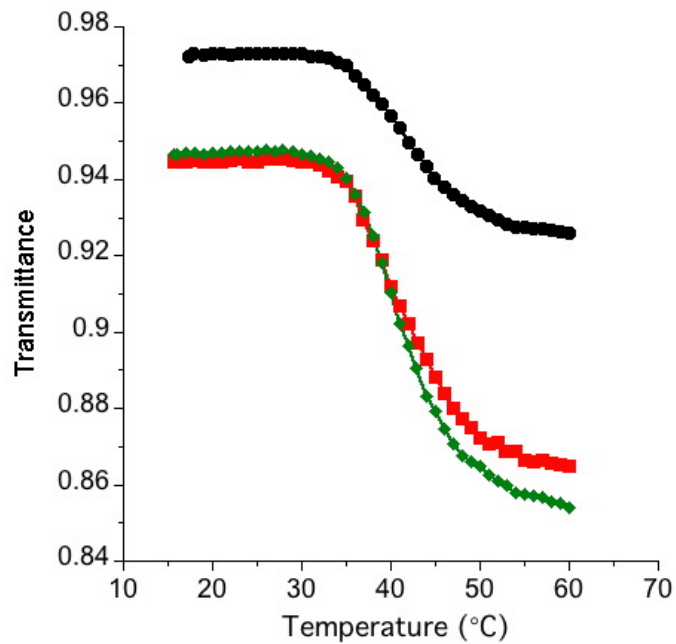


Figure S 15. Transmittance versus temperature plot of PNIPAAm₇₂-PBPN₂₆. Runs 1 (●), 2, (◻), and 3 (◊). (0.2 mg/mL, DI Water).

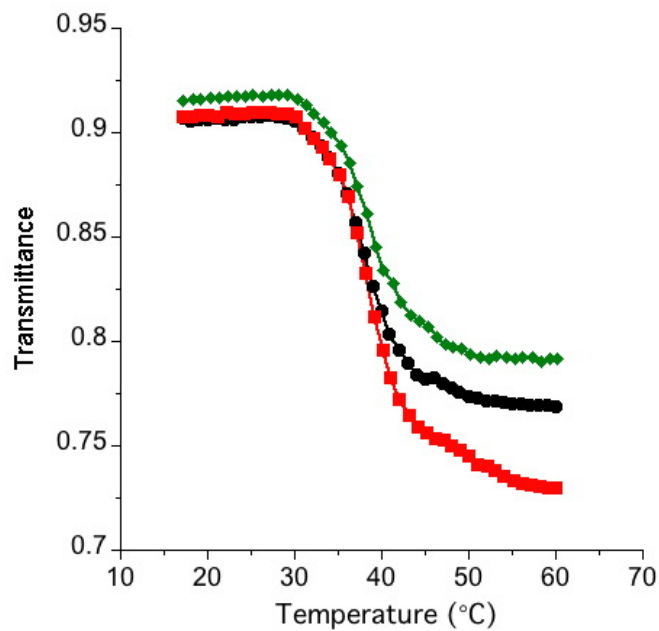


Figure S 16. Transmittance versus temperature plot of PNIPAAm₇₂-PBPN₇₃. Runs 1 (●), 2, (◻), and 3 (◊). (0.2 mg/mL, DI Water).

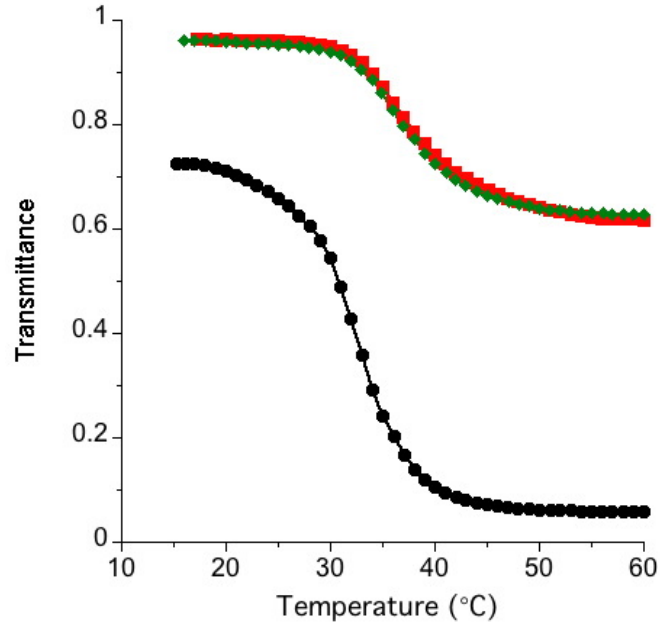


Figure S 17. Transmittance versus temperature plot of PNIPAAm₇₂-PMNP₂₉. Runs 1 (●), 2, (◻), and 3 (◊). (0.2 mg/mL, DI Water).

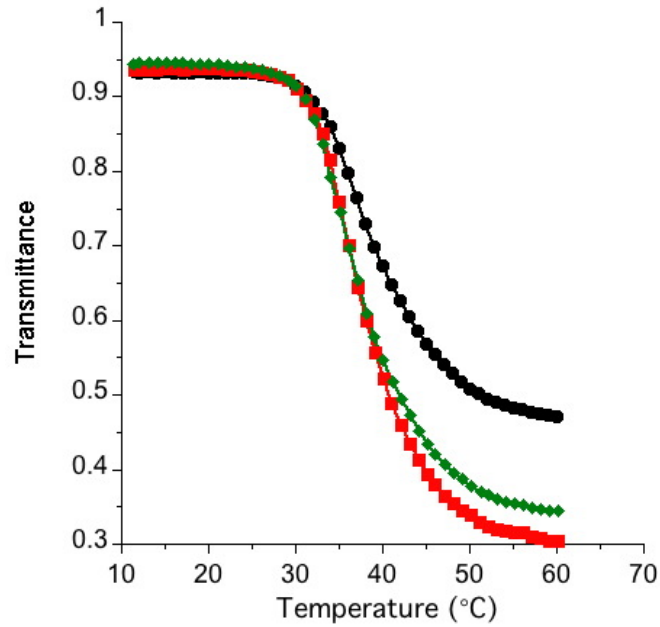


Figure S 18. Transmittance versus temperature plot of PNIPAAm₇₂-PMNP₇₈. Runs 1 (●), 2, (◻), and 3 (◊). (0.2 mg/mL, DI Water).

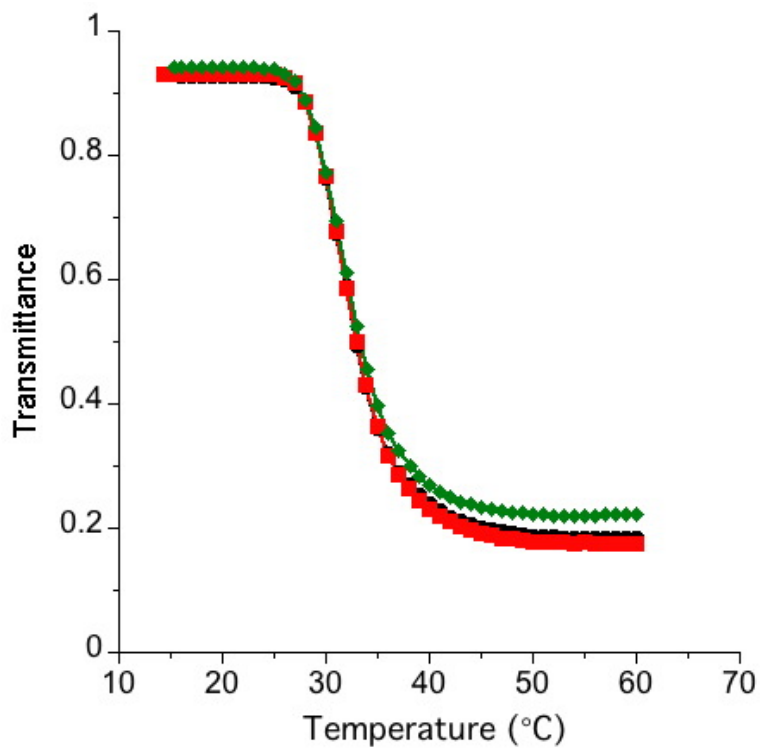


Figure S 19. Transmittance versus temperature plot of PNIPAAm₇₂-PNP₂₉. Runs 1 (●), 2, (⊙), and 3 (⊕). (0.2 mg/mL, DI Water).

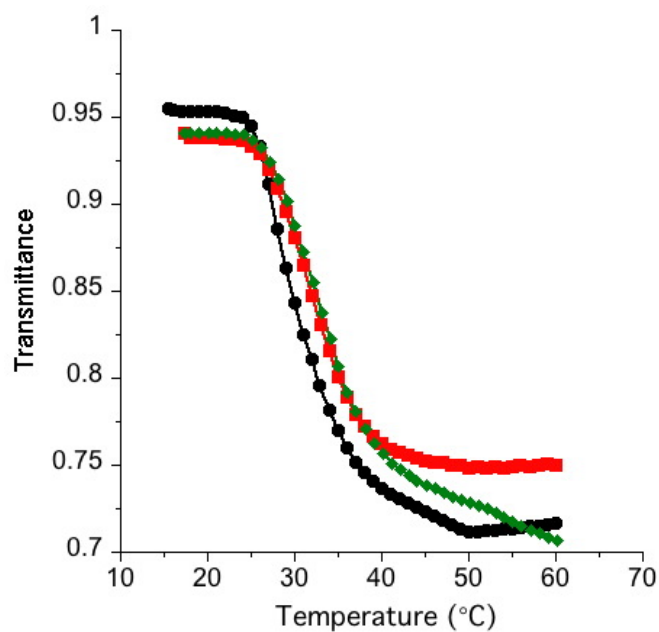


Figure S 20. Transmittance versus temperature plot of PNIPAAm₇₂-PNP₇₃. Runs 1 (●), 2, (⊙), and 3 (⊕). (0.2 mg/mL, DI Water).

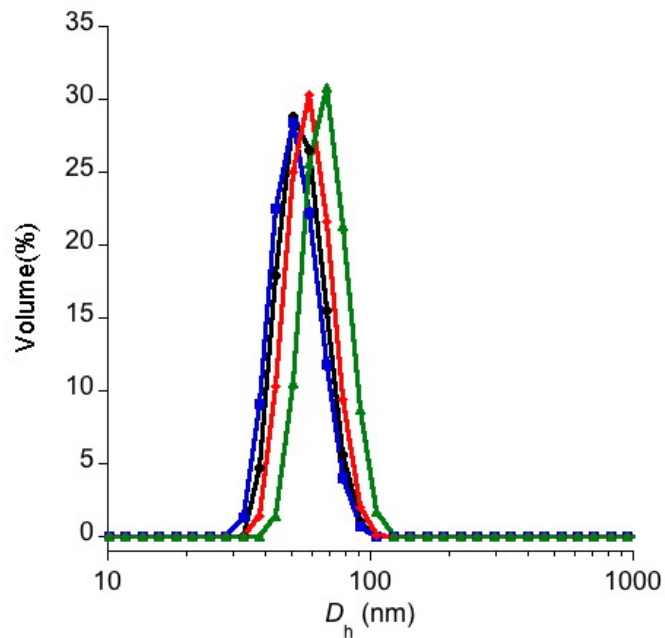


Figure S 21. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₂₆ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (◻). Run 1.

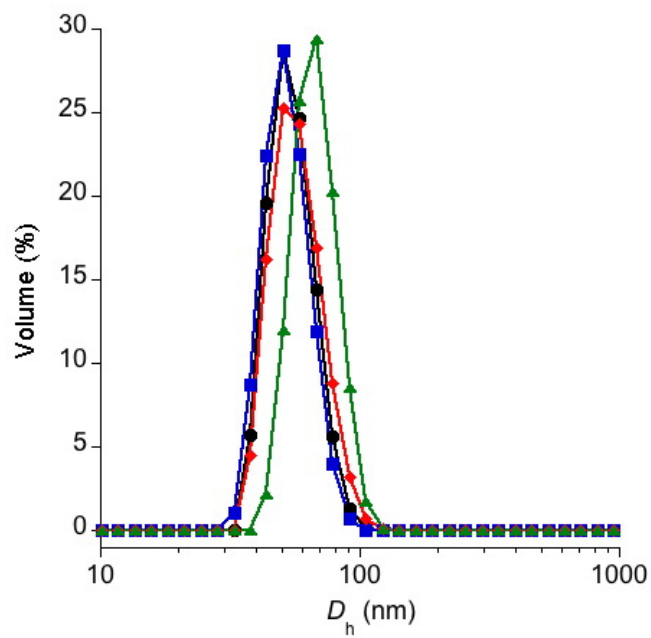


Figure S 22. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₂₆ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (◻). Run 2.

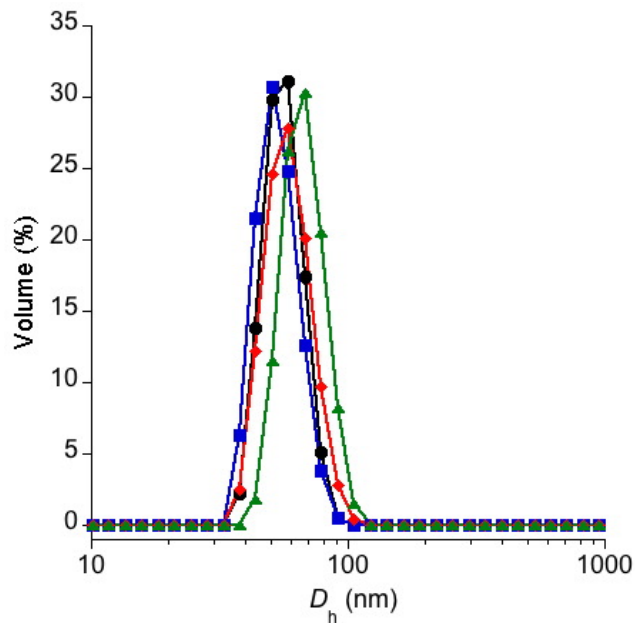


Figure S 23. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₂₆ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 3.

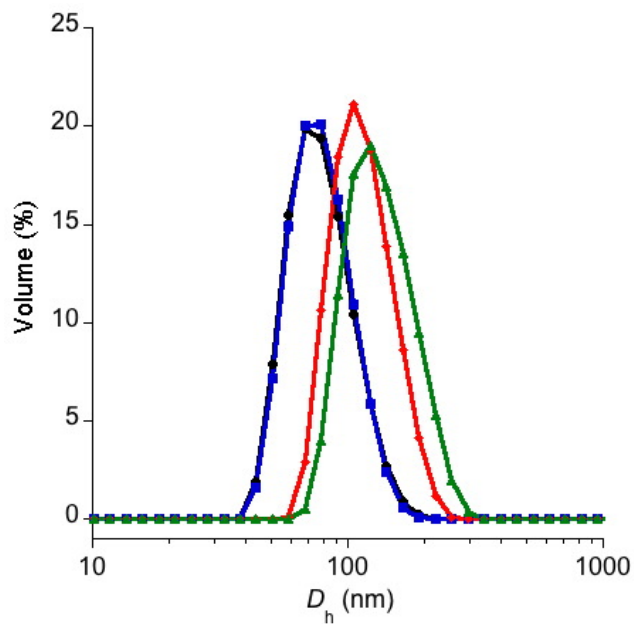


Figure S 24. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₂₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 1.

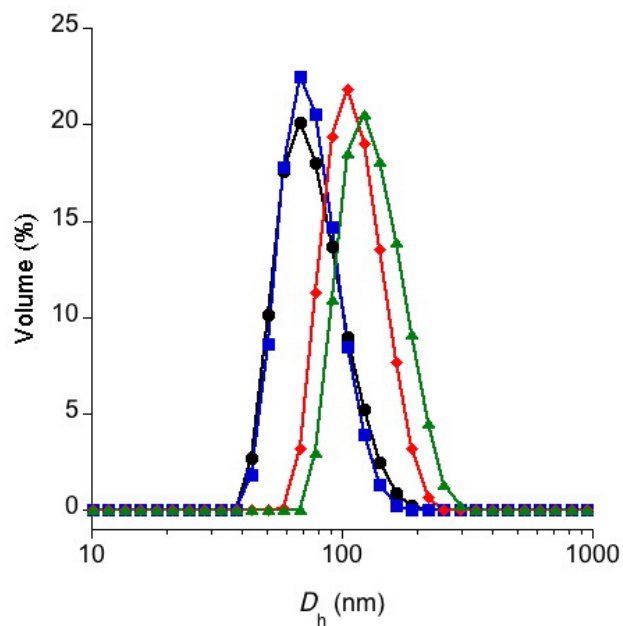


Figure S 25. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₂₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊖). Run 2.

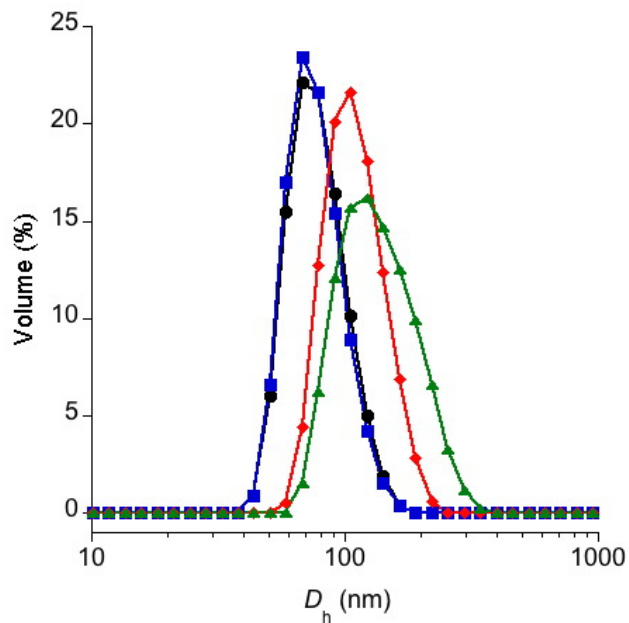


Figure S 26. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₂₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊖). Run 3.

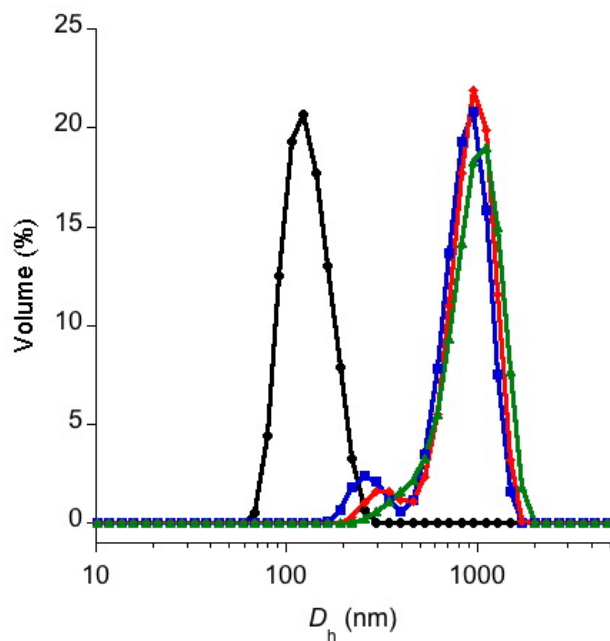


Figure S 27. Hydrodynamic diameter (D_h) distribution (Volume %) of PNIPAAm₇₂-PNP₂₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 1.

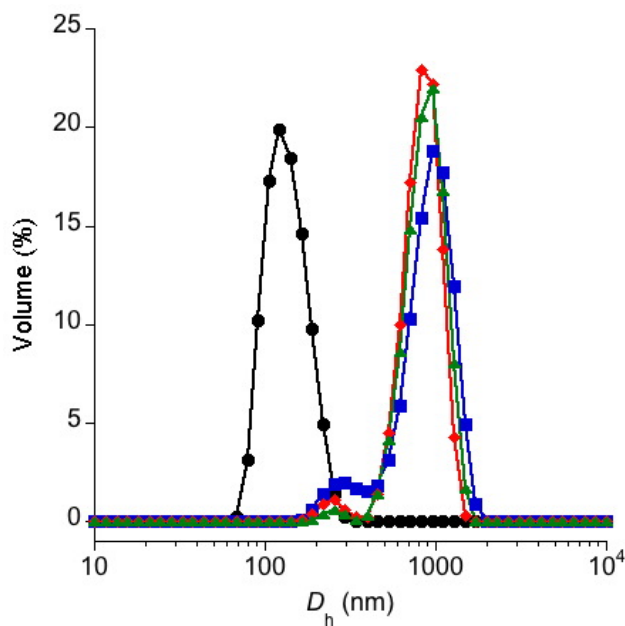


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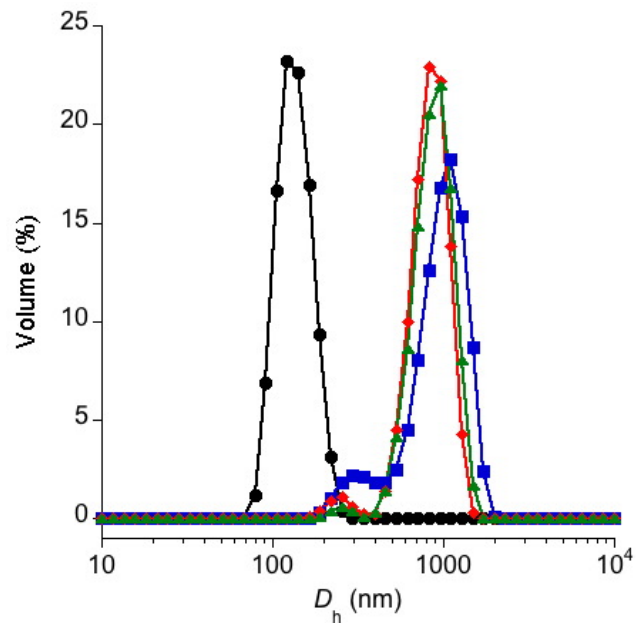


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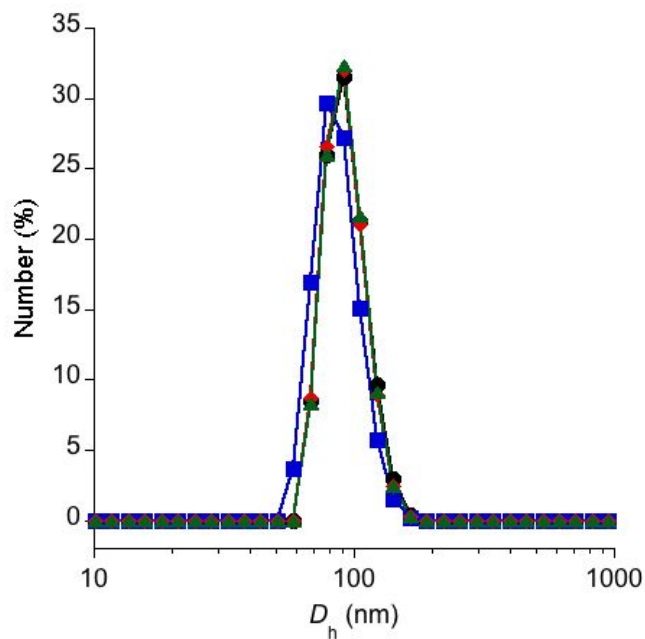


Figure S 30. Hydrodynamic diameter (D_h) distribution (Number (%)) of PNIPAAm₇₂-PBNP₇₃ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙).

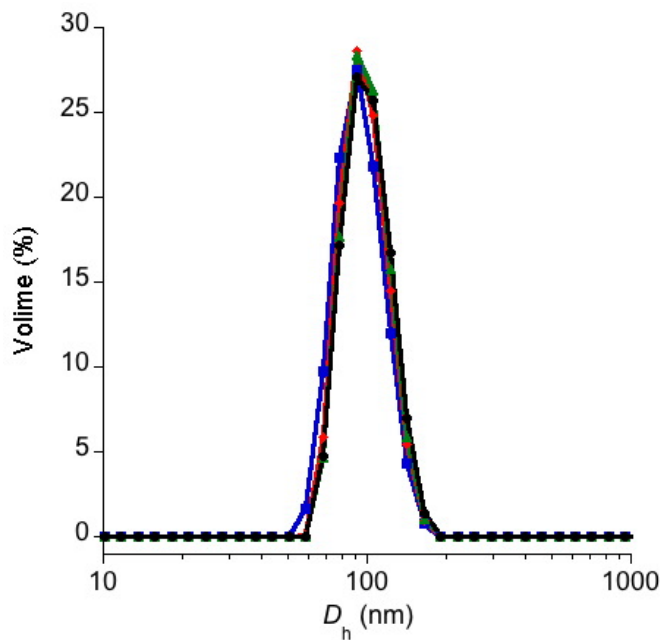


Figure S 31. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₇₃ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 1.

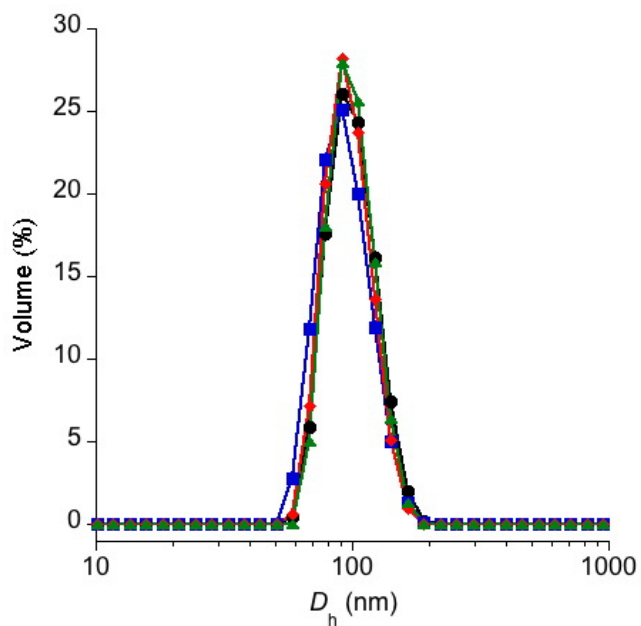


Figure S 32. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PBNP₇₃ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 2.

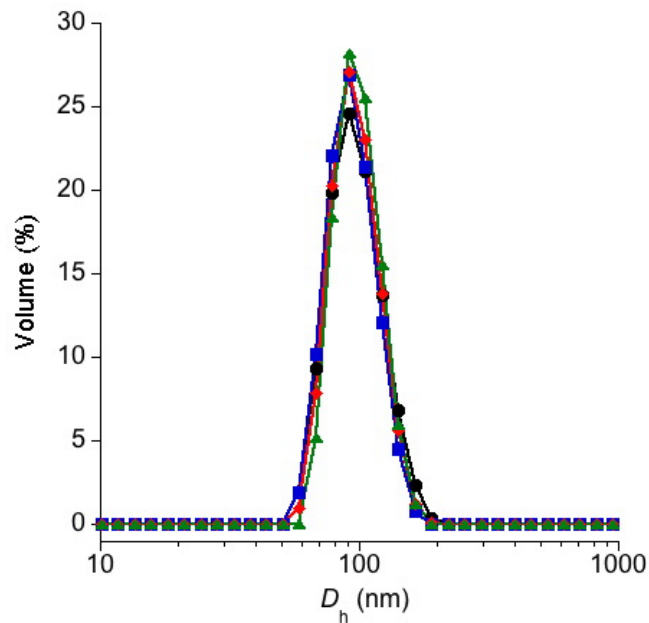


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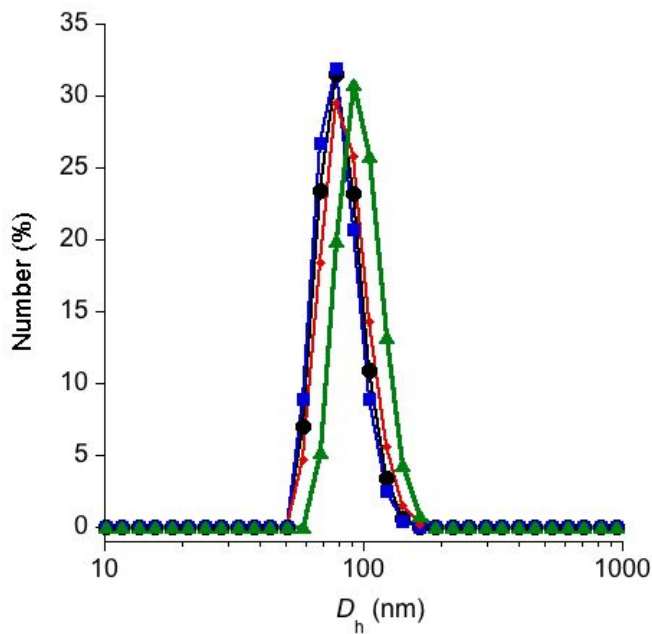


Figure S 34. Hydrodynamic diameter (D_h) distribution (Number (%)) of PNIPAAm₇₂-PMNP₇₈ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊕).

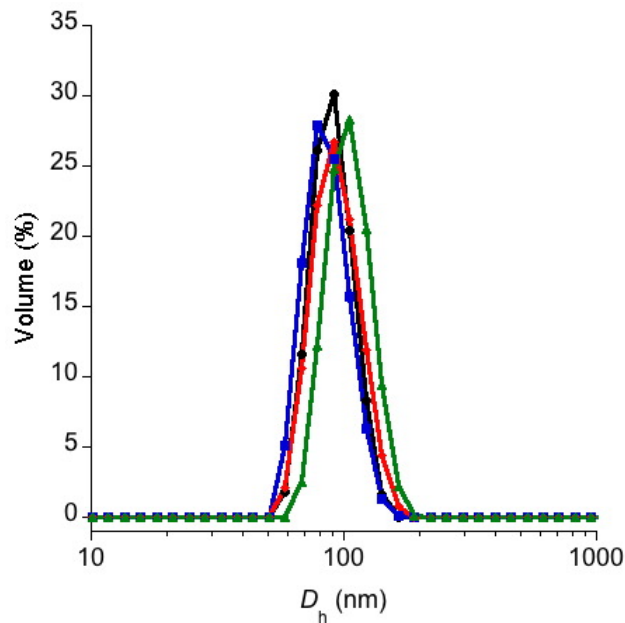


Figure S 35. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₇₈ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 1.

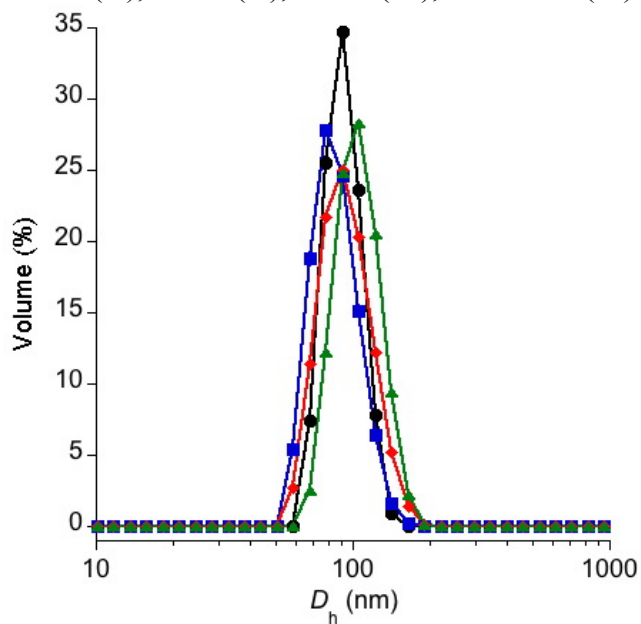


Figure S 36. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₇₈ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 2.

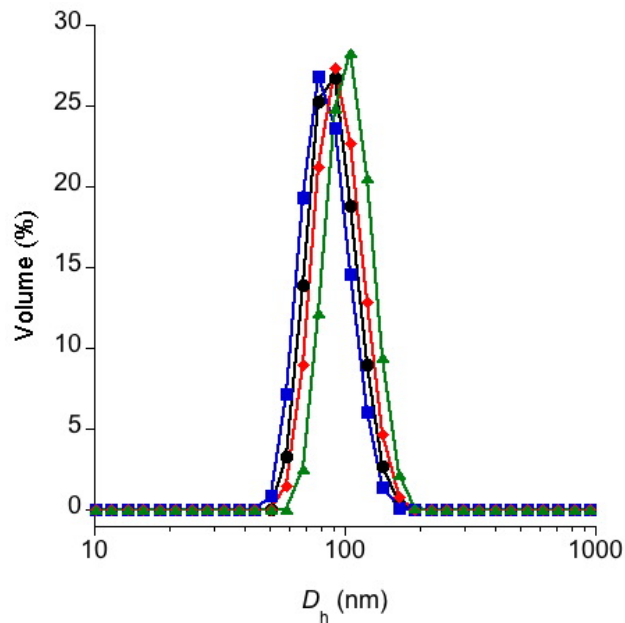


Figure S 37. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PMNP₇₈ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 3.

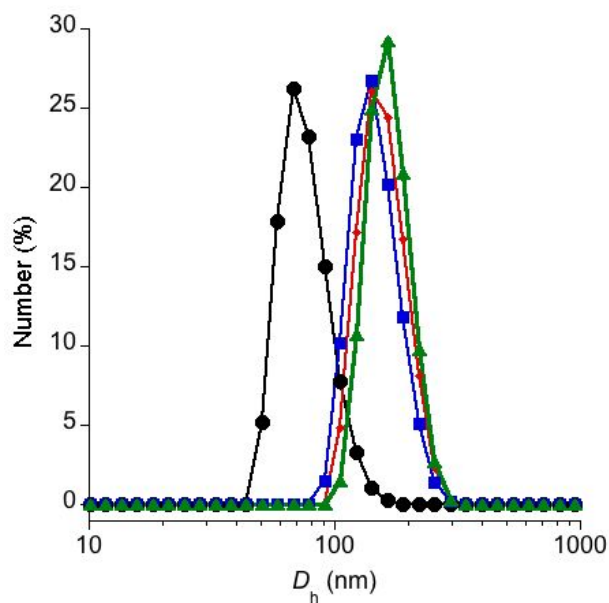


Figure S 38. Hydrodynamic diameter (D_h) distribution (Number (%)) of PNIPAAm₇₂-PNP₇₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙).

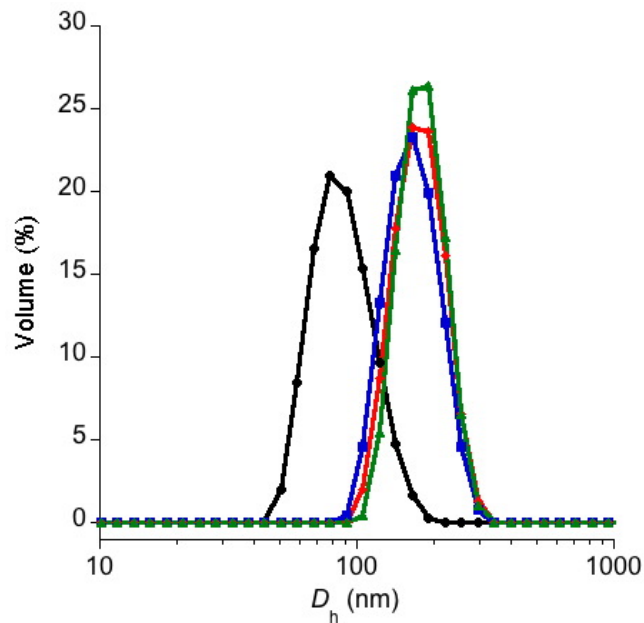


Figure S 39. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PNP₇₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊖). Run 1.

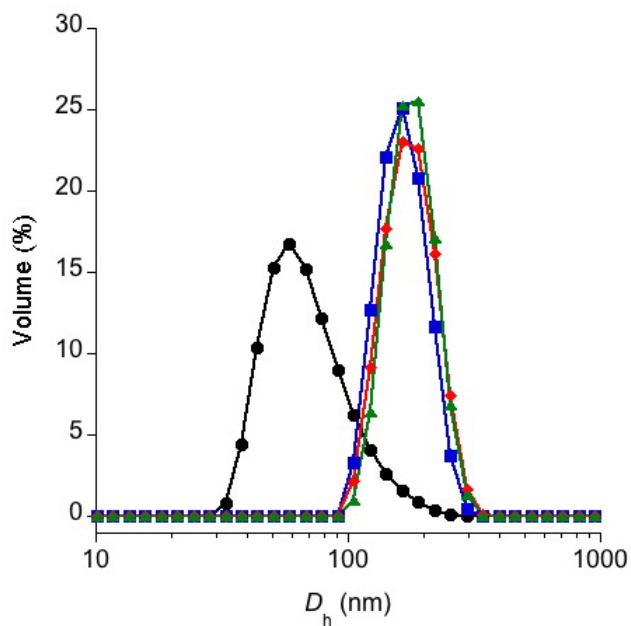


Figure S 40. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PNP₇₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊖). Run 2.

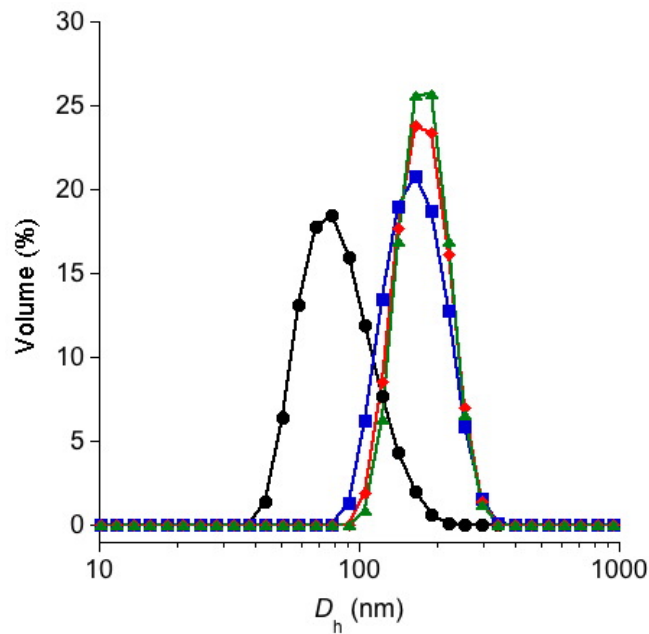


Figure S 41. Hydrodynamic diameter (D_h) distribution (Volume (%)) of PNIPAAm₇₂-PNP₇₉ micelles at 25 °C (●), 35 °C (■), 40 °C (◆), and 50 °C (⊙). Run 3.

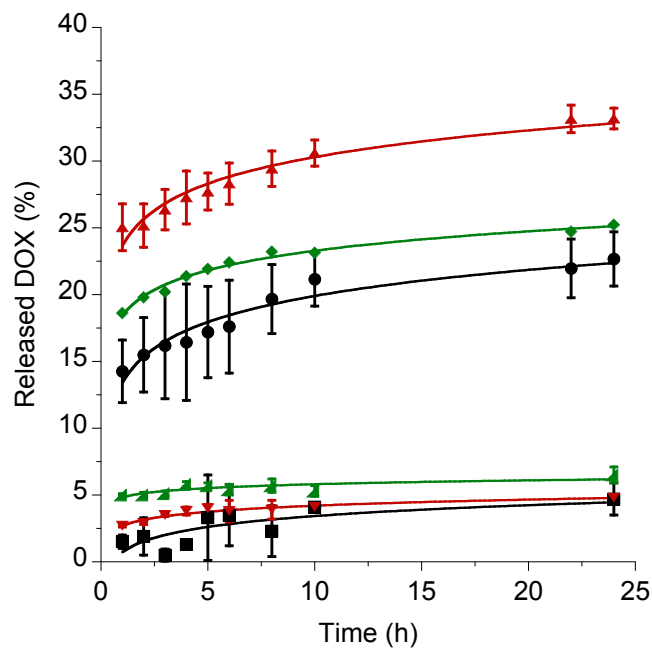


Figure S 42. DOX release from a) PNIPAAm₇₂-PNP₇₉ at 37°C (⊙) and 20°C (⊚), PNIPAAm₇₂-PMNP₇₈ at 37°C (◆) and 20°C (⊞), and PNIPAAm₇₂-PBNP₇₃ 37°C (●) and 20°C (⊙). Data points are plotted as a mean with standard deviation (n = 3).

Table S1. LCST (°C) of block copolymers in deionized water.

Polymer	Run 1	Run 2	Run 3
PNIPAAm ₇₂ -PBNP ₇₃	34.9	37.9	39.9
PNIPAAm ₇₂ -PBNP ₂₆	41.9	40.9	40.9
PNIPAAm ₇₂ -PMNP ₇₈	39.0	38.0	38.9
PNIPAAm ₇₂ -PMNP ₂₉	37.9	37.0	39.9
PNIPAAm ₇₂ -PNP ₇₉	32.0	34.1	32.2
PNIPAAm ₇₂ -PNP ₂₉	32.9	32.9	31.9

Table S2. LCST (°C) of block copolymers in PBS solution.

Polymer	Run 1	Run 2	Run 3	mean ± S.D.
PNIPAAm ₇₂ -PBNP ₇₃	34.0	33.0	34.0	33.6 ± 0.6
PNIPAAm ₇₂ -PBNP ₂₆	31.9	32.9	32.1	32.3 ± 0.5
PNIPAAm ₇₂ -PMNP ₇₈	33.1	33.2	32.1	32.8 ± 0.6
PNIPAAm ₇₂ -PMNP ₂₉	33.1	33.0	33.1	33.1 ± 0.0
PNIPAAm ₇₂ -PNP ₇₉	25.0	28.1	26.3	26.5 ± 1.6
PNIPAAm ₇₂ -PNP ₂₉	28.0	28.1	28.0	28.0 ± 0.0

Table S3. D_h of micelles (Volume (%)) with PDI in parentheses.

Polymer	Run 1	Run 2	Run 3	mean ± S.D.
PNIPAAm ₇₂ -PBNP ₇₃	101.5 (0.019)	101.5 (0.025)	98.9 (0.050)	100.6 ± 1.5
PNIPAAm ₇₂ -PBNP ₂₆	55.7 (0.027)	55.3 (0.043)	56.7 (0.034)	55.9 ± 0.7
PNIPAAm ₇₂ -PMNP ₇₈	91.1 (0.041)	92.7 (0.002)	90.9 (0.038)	91.6 ± 1.0
PNIPAAm ₇₂ -PMNP ₂₉	80.7 (0.098)	78.4 (0.074)	79.9 (0.068)	79.7 ± 1.2
PNIPAAm ₇₂ -PNP ₂₉	131.3 (0.125)	138.2 (0.077)	138.2 (0.057)	135.9 ± 4.0
PNIPAAm ₇₂ -PNP ₇₉	90.4 (0.119)	73.2 (0.131)	85.8 (0.121)	83.1 ± 8.9

Table S4. D_h of drug-loaded micelles (Volume (%)) with PDI in parentheses.

Polymer	Run 1	Run 2	Run 3	mean ± S.D.
PNIPAAm ₇₂ -PBNP ₇₃	56.6 (0.253)	52.2 (0.256)	58.3 (0.252)	55.7 ± 3.1
PNIPAAm ₇₂ -PBNP ₂₆	36.0 (0.172)	37.4 (0.156)	35.9 (0.159)	36.5 ± 0.8
PNIPAAm ₇₂ -PMNP ₇₈	45.4 (0.240)	57.7 (0.236)	56.4 (0.265)	53.0 ± 6.6
PNIPAAm ₇₂ -PMNP ₂₉	55.0 (0.199)	47.5 (0.201)	65.4 (0.191)	55.9 ± 9.0
PNIPAAm ₇₂ -PNP ₂₉	78.3 (0.243)	75.3 (0.226)	80.8 (0.108)	78.1 ± 2.8
PNIPAAm ₇₂ -PNP ₇₉	143.4 (0.141)	141.2 (0.135)	144.7 (0.145)	143.1 ± 1.8