

Electronic Supporting Information

Inverse Miniemulsion Periphery RAFT Polymerization: A Convenient Route to Hollow Polymeric Nanoparticles with an Aqueous Core

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Theoretical Calculation of Shell Thickness

A representative calculation of the theoretical shell thickness is shown herein. This calculation corresponds to the hollow polymeric nanoparticles comprising MMA/EGDMA shell (**R2 with** (poly(HPMA-*b*-MMA) as the macroRAFT stabilizer).

Theoretical Maximum Based on the Contour Length

The number of C-C bond in the hydrophobic (MMA) segment of the macroRAFT stabilizer (N_{MMA}) is calculated as follow:

$$\begin{aligned} N_{\text{MMA}} &= \frac{[\text{MMA}]}{[\text{RAFT}]} \times \text{Conversion} \times 2 \\ &= 200 \times 0.4 \times 2 = 160 \end{aligned}$$

Similarly, the number of C-C bond of the crosslinked block synthesized during the miniemulsion polymerization is:

$$N_{\text{IMEPP}} = (200 \times 0.51 \times 2) + (25 \times 0.51 \times 2) = 229.5$$

Hence, the theoretical maximum shell thickness is the sum of the contour length of the MMA segment from the stabilizer and the crosslinked block:

$$\text{Thickness} = (160 \times 0.154 \times \sin(54.5)) + (229.5 \times 0.154 \times \sin(54.5))$$

$$\text{Thickness} = 48.83 \text{ nm}$$

Theoretical Minimum Based on the Volume of the Polymerized Monomer

Initially, the diameter of the “naked” droplet (d_d) is calculated by subtracting the initial diameter of the droplet (d_n , 170 nm) with the maximum contour length of the hydrophobic segment of the macroRAFT stabilizer (40.12 nm, accounting for both sides):

$$d_d = 170 - 40.12 = 129.88 \text{ nm}$$

The calculated “naked” droplet volume is:

$$V_{\text{droplet}} = \frac{4}{3} \times \pi \times \left(\frac{129.88}{2}\right)^3$$

$$V_{\text{droplet}} = 1.15 \times 10^6 \text{ nm}^3$$

The number of droplets in the system is based on the volume of dispersed phase ($V_{\text{dispersed phase}}$; $1.3 \times 10^9 \text{ nm}^3$) and calculated as follow:

$$\text{Total number of droplets} = 1.3 \times 10^9 \div 1.15 \times 10^6$$

$$\text{Total number of droplets} = 1133.22$$

The total volume of all nanoparticles (V_{total}) would be then the sum of the $V_{\text{dispersed phase}}$, the volume of the hydrophobic segment within the macroRAFT stabilizer ($V_{\text{hydrophobic}}$);

$$V_{\text{hydrophobic}} = \frac{n_{\text{stabilizer}}}{M_{\text{hydrophobic}}} \times \rho_{\text{MMA}}$$

$$V_{\text{hydrophobic}} = \frac{1.18 \times 10^5}{8000} \times 0.94$$

$$V_{\text{hydrophobic}} = 1.004 \times 10^8 \text{ nm}^3$$

and the volume of the crosslinked block due to miniemulsion polymerization (V_{IMEPP});

$$V_{\text{IMEPP}} = \text{Conversion} \times (V_{\text{monomer,IMEPP}} + V_{\text{Crosslinker,IMEPP}})$$

$$V_{\text{IMEPP}} = 0.51 \times (2.52 \times 10^8 + 5.62 \times 10^7)$$

$$V_{\text{IMEPP}} = 1.57 \times 10^8 \text{ nm}^3$$

to give:

$$V_{\text{Total}} = 1.3 \times 10^9 + 1.004 \times 10^8 + 1.57 \times 10^8$$

$$V_{\text{total}} = 1.56 \times 10^9 \text{ nm}^3$$

The volume of the individual nanoparticle (V_p) is calculated as follow:

$$V_p = 1.56 \times 10^9 \div 1133.22 = 1.37 \times 10^6 \text{ nm}^3$$

The diameter of the nanoparticles (d_p) is:

$$d_p = 2 \times \left(\frac{3}{4} \times \frac{1.37 \times 10^6}{\pi} \right)^{\frac{1}{3}} = 137.94 \text{ nm}$$

Finally, the minimum theoretical shell thickness is:

$$\text{Shell Thickness} = \frac{137.94 - 129.88}{2} = 4.03 \text{ nm}$$

Quantification of the Pendant Conversion

The following calibration is used to determine the pendant conversion.

Table S1. Bromine standards used for calibration

| Sample ID | [Br ₂] (mol L ⁻¹) | Intensity (a.u) |
|------------|---|-----------------|
| Standard 1 | 0.0019 | 0.1869 |
| Standard 2 | 0.0029 | 0.2180 |
| Standard 3 | 0.0039 | 0.3530 |
| Standard 4 | 0.0058 | 0.5088 |
| Standard 5 | 0.0068 | 0.6420 |
| Standard 6 | 0.0078 | 0.7667 |

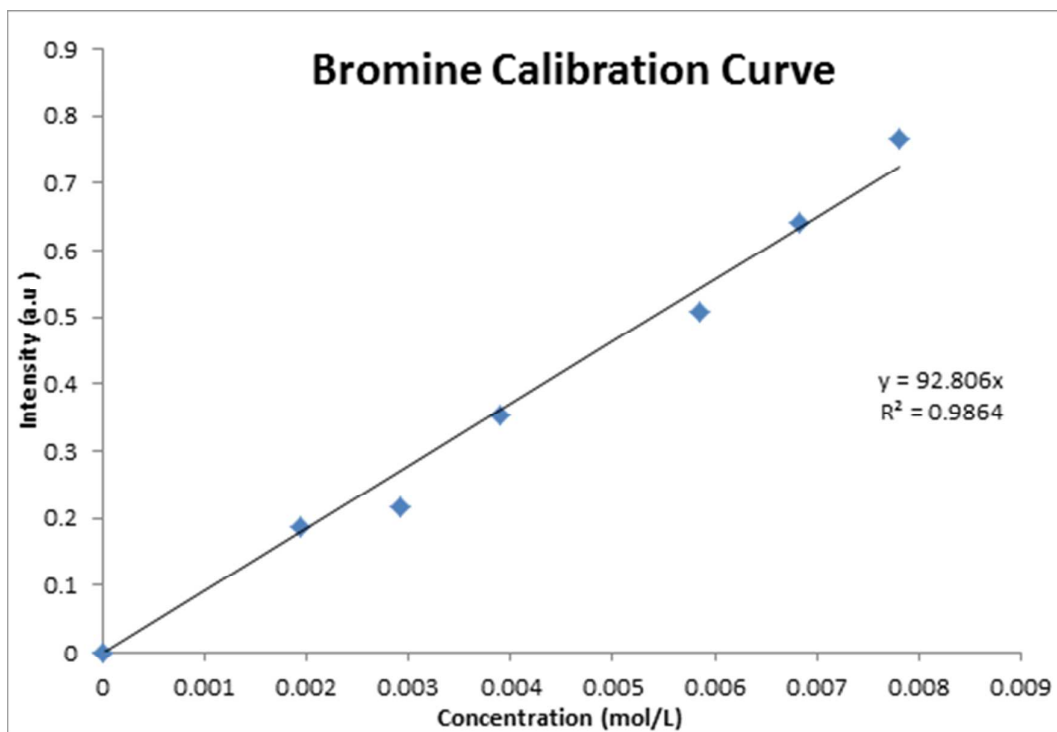


Figure S1. Bromine solution calibration curve

For the control experiment (the bromination of the macroRAFT stabilizer), the following table summarises the raw data used and the calculated results.

Table S2. Experimental data and calculated results for bromination of the macroRAFT stabilizer, showing the mole ratio of bromine reacted with the macroRAFT stabilizer.

| | | | |
|--|-----------------------|-----------------------|---|
| Time (h) | 0 | 2 | Note |
| Br₂ peak intensity (a.u) | 0.7078 | 0.6761 | |
| [Br₂] (mol L⁻¹) | 0.007627 | 0.0072848 | |
| V_{sample} (L) | 0.005 | | |
| n_{Br} (mol) | 3.81×10^{-5} | 3.64×10^{-5} | $n_{Br} = [Br_2] \times V_{sample}$ |
| n_{Br,reacted} (mol) | 1.71×10^{-6} | | $n_{Br, reacted} = n_{Br,0} - n_{Br, 2}$ |
| m_{block copolymer} (g) | 0.0203 | | |
| M_{block copolymer} (g/mol) | 11,000 | | |
| n_{block copolymer} (g) | 1.84×10^{-6} | | |
| Ratio | 0.926 | | $Ratio = n_{Br, reacted} / n_{block copolymer}$ |

For every sample analysed, the molecular weight of each tri-block copolymer (assuming no crosslinking) is calculated. These values were used to calculate the number of moles of specific segment of the polymeric shell.

Table S3. Molecular weight of the individual segment of the un-crosslinked block copolymer, synthesized *via* IMEPP of the macroRAFT stabilizer, and the total molecular weight of the overall block copolymer

| Sample ID | M of macroRAFT (g/mol) | Conversion (%) | $M_{MMA, Shell}$ (g/mol) | MMA repeating unit ($\#_{MMA}$) | $M_{EGDMA, Shell}$ (g/mol) | EGMDA repeating unit ($\#_{EGDMA}$) | M_{total} (g/mol) |
|-----------|--------------------------|----------------|--------------------------|-----------------------------------|----------------------------|---------------------------------------|---------------------|
| R3 | 11,000 | 12 | 2,400 | 24 | 600 | 3 | 14,000 |
| R4 | 11,000 | 25 | 5,010 | 50 | 1,240 | 6 | 17,250 |
| R5 | 11,000 | 48 | 9,610 | 96 | 2,380 | 12 | 22,990 |
| R6 | 11,000 | 29 | 13,060 | 130 | 2,590 | 13 | 26,650 |
| R7 | 11,000 | 72 | 32,450 | 324 | 6,420 | 32 | 49,870 |

Finally, the pendant conversion is calculated. The resulting raw data from the UV-Vis analysis and the calculation results are summarized below.

Table S4. Experimental data and calculated results of the bromination of various synthesized NPs (R3-R7), showing the pendant conversion of each nanoparticles.

| Sample ID | R3 | | R4 | | R5 | |
|---|-------------------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|
| | 0 | 2 | 0 | 2 | 0 | 2 |
| Time (h) | 0 | 2 | 0 | 2 | 0 | 2 |
| Br ₂ peak intensity (a.u) | 0.1378 | 0.0878 | 0.2112 | 0.1427 | 0.4419 | 0.3799 |
| [Br ₂] (mol L ⁻¹) | 1.4x10 ⁻³ | 9.5x10 ⁻⁴ | 2.3x10 ⁻³ | 1.5x10 ⁻³ | 4.8x10 ⁻³ | 4.1x10 ⁻³ |
| V _{sample} (L) | 0.005 | | 0.005 | | 0.005 | |
| n _{Br} (mol) | 7.4x10 ⁻⁶ | 4.7x10 ⁻⁶ | 1.1x10 ⁻⁵ | 7.7x10 ⁻⁶ | 2.4x10 ⁻⁵ | 2.0x10 ⁻⁶ |
| n _{Br, Reacted} (mol) | 2.69 x 10 ⁻⁶ | | 3.69x10 ⁻⁶ | | 3.34x10 ⁻⁶ | |
| m _{NPs} (g) | 0.0123 | | 0.0176 | | 0.015 | |
| n _{EGDMA} (g/mol) | 2.64x10 ⁻⁶ | | 6.38x10 ⁻⁶ | | 7.83x10 ⁻⁶ | |
| n _{BrBC} (g/mol) | 8.14x10 ⁻⁷ | | 9.45x10 ⁻⁷ | | 6.04x10 ⁻⁷ | |
| n _{BrEGDMA} (g/mol) | 1.88x10 ⁻⁶ | | 2.75x10 ⁻⁶ | | 2.73x10 ⁻⁶ | |
| Pendant conversion (%) | 28.6 | | 56.9 | | 65.4 | |

| Sample ID | R6 | | R7 | | Note |
|---|-------------------------|----------------------|-----------------------|----------------------|--|
| | 0 | 2 | 0 | 2 | |
| Time (h) | 0 | 2 | 0 | 2 | |
| Br ₂ peak intensity (a.u) | 0.4681 | 0.4044 | 0.4575 | 0.3894 | |
| [Br ₂] (mol L ⁻¹) | 5.0x10 ⁻³ | 4.4x10 ⁻⁴ | 4.9x10 ⁻³ | 4.2x10 ⁻³ | |
| V _{sample} (L) | 0.005 | | 0.005 | | |
| n _{Br} (mol) | 2.5x10 ⁻⁵ | 2.2x10 ⁻⁵ | 2.5x10 ⁻⁵ | 2.1x10 ⁻⁶ | n _{Br} = [Br ₂] x V _{sample} |
| n _{Br, Reacted} (mol) | 3.43 x 10 ⁻⁶ | | 3.67x10 ⁻⁶ | | n _{Br} = n _{Br,0} - n _{Br, 2} |
| m _{NPs} (g) | 0.0161 | | 0.0297 | | |
| n _{EGDMA} (g/mol) | 7.88x10 ⁻⁶ | | 1.93x10 ⁻⁵ | | n _{EGDMA} = (m _{NPs} / M _{total}) x # _{EGDMA} |
| n _{BrBC} (g/mol) | 5.60x10 ⁻⁷ | | 5.52x10 ⁻⁷ | | n _{BrBC} = (m _{NPs} / M _{total}) x Ratio |
| n _{BrEGDMA} (g/mol) | 2.87x10 ⁻⁶ | | 3.11x10 ⁻⁶ | | n _{BrEGDMA} = n _{Br, Reacted} - n _{BrBC} |
| Pendant conversion (%) | 63.6 | | 83.9 | | |

