Supporting Information for

Emulsion and Nanocapsules of Ternary Graft Copolymers

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Materials. CuBr (98%), $CuSO_4 \cdot 5H_2O$ (99%), sodium ascorbate (SA, 99%), disodium ethylenediamine tetraacetate (EDTA, 99%), tetrabutylammonium fluoride (TBAF, 98%), *tert*-butyl acrylate (tBA, 99%), methylbenzene (99%), decahydronaphthalene (DN, 99%), *N,N*-dimethylformamide (DMF, 99%), *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, 99%), tetrahydrofuran (THF, 99%), dichloromethane (DCM, 99%), and methanol (99%) were all purchased from Aladdin Reagents of China. CuBr was purified by rinsing this reagent with glacial acetic acid, methanol, and diethyl ether before it was dried under vacuum. $CuSO_4 \cdot 5H_2O$, SA, EDTA, DN, DMF, THF, DCM, and methanol were used as received. Methylbenzene was refluxed over CaH_2 overnight and distilled prior to use. *Tert*-butyl acrylate was washed three times with an equal volume of a 5 wt% NaOH aqueous solution during each wash and then washed with water until the water

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phase was neutral. This solution was dried over anhydrous sodium sulfate and then distilled under reduced pressure. *N*-Hydroxysuccinimide (NHS, 98%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimidemethiodide (EDC·CH_3I, 97%), and 2,2'-(ethylenedioxy)bis(ethylamine) (98%) were purchased from Aldrich and used as received. 3-(Trimethylsilyl)propargyl 2-bromoisobutyrate were synthesized according to literature procedures.[29] $P(GMA-N_3)_{41}$, $MPEG_{114}$-C≡CH, PS_{40}-C≡CH and PS_{130}-C≡CH (with subscripts denoting the number of repeat units) were prepared and characterized according to our recently-reported procedures.[28] All other reagents and solvents were used as received unless otherwise specified.

PtBA-C≡CH. $PtBA_{142}$-C≡C-TMS was prepared via ATRP using 3-(trimethylsilyl)propargyl 2-bromoisobutyrate as the initiator. Methylbenzene (25.0 mL), 3-(trimethylsilyl)propargyl 2-bromoisobutyrate (0.188 g, 0.678 mmol), *tert*-butyl acrylate (25.20 g, 0.196 mol), CuBr (0.097 g, 0.678 mmol), and a magnetic stirring bar were placed inside a 100 mL round-bottom flask. The flask was subjected to an "evacuate and argon back-filling" process thrice before it was subsequently deoxygenated by two "freeze, evacuate, thaw, and argon fill" cycles. PMDETA (0.118 g, 0.678 mmol) was injected into the flask using a degassed syringe and the flask was then immersed into a pre-heated oil bath at 80 °C. The reaction was performed for 6.0 h before the flask was immersed into liquid nitrogen and its contents were exposed to air. The mixture was diluted by adding 100 mL of THF. This solution was subsequently passed through an activated neutral alumina column before the filtrate was concentrated to ~30 mL via rotary evaporation and added into

500 mL of a 7:3 (v/v) mixture of methanol/water to precipitate the polymer. The polymer was re-dissolved into ~30 mL of THF and subsequently precipitated from 500 mL of a 7:3 (v/v) mixture of methanol/water again. The precipitate was dried under vacuum for 24 h, yielding 11.6 g of PtBA-C≡C-TMS in a 46 wt% yield. The average degree of polymerization (*DP*) for PtBA-C≡C-TMS was 142 as evaluated from ^{1}H NMR spectra recorded in $CDCl_3$ by comparison of the proton integration of the C≡CC*H₂*- signal at 4.64 ppm to that of the $-CH_2C\mathit{H}-$ signal at 2.19 ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64 (s, $-CH_2O-$), 2.22 (br, $-CH_2C\mathit{H}-$), 1.84 (br, $-C\mathit{H_2}CH-$), 1.53 (br, $-C\mathit{H_2}CH-$), 1.44 (br, $-C(CH_3)_3-$), 0.15 ($-Si(CH_3)_3$).

$PtBA_{60}$-C≡C-TMS was prepared in a similar manner, except that a different *tert*-butyl acrylate-to-initiator molar ratio was used. The yield of the final polymer was 52 %.

To remove the trimethylsilyl protecting group from the initiating unit, 8.0 g of either $PtBA_{142}$-C≡C-TMS or $PtBA_{60}$-C≡C-TMS that had been prepared during the previous step along with DMF (30 mL) and tetrabutylammonium fluoride (5.0 g, 0.019 mol) were stirred together at room temperature for 48 h in a 100 mL flask. After most of the solvent was removed under reduced pressure, the remaining solution (~10 mL) was added to 500 mL of a 7:3 (v/v) methanol/water solvent mixture to precipitate the polymer and remove any residual salts. The obtained product was dried under vacuum for 24 h, thus generating 7.3 g of PtBA-C≡CH in a 91 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64 (s, $-CH_2O-$), 2.22 (br, $-CH_2C\mathit{H}-$), 1.84(br, $-C\mathit{H_2}CH-$), 1.53 (br, $-C\mathit{H_2}CH-$), 1.44 (br, $-C(CH_3)_3-$).

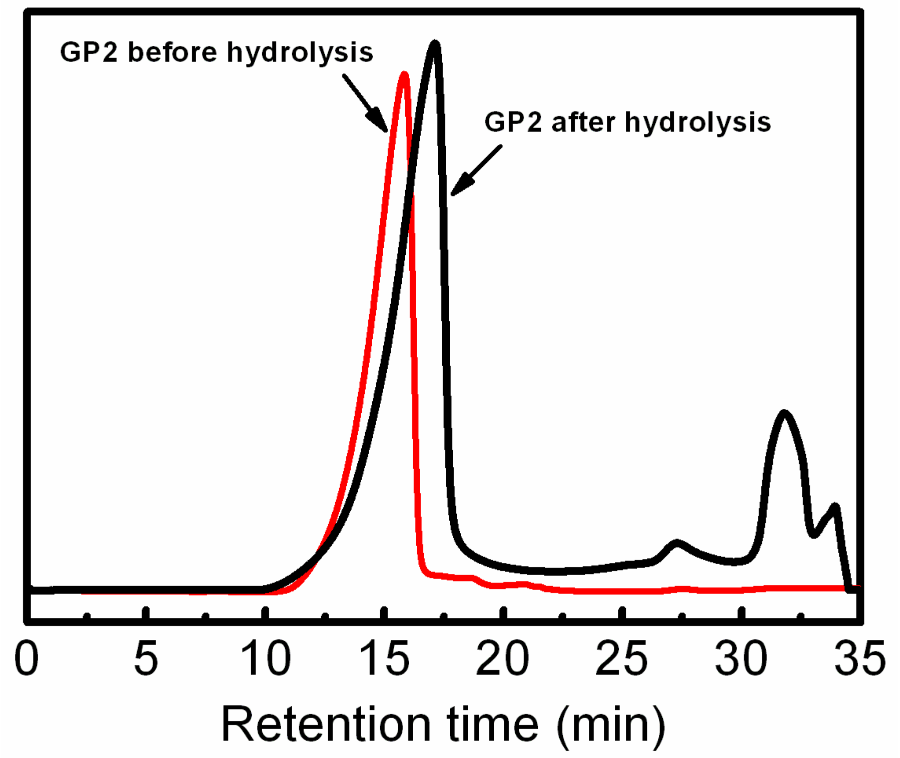

Figure S1. SEC traces of GP2 before and after TFA hydrolysis. DMF was used as the mobile phase.

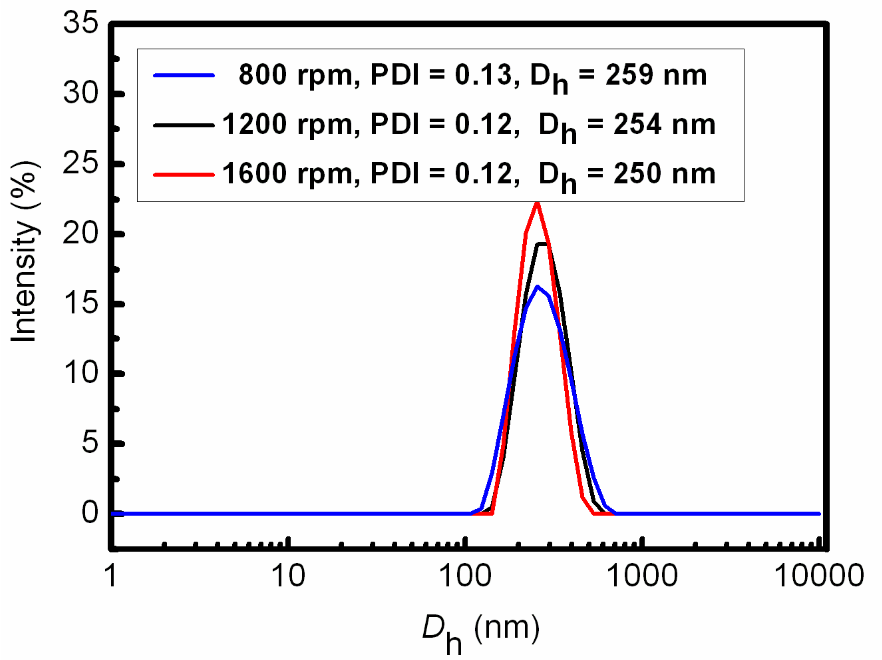

Figure S2. DLS size distribution plot for nanocapsules fabricated from GP1 at various stirring rates.

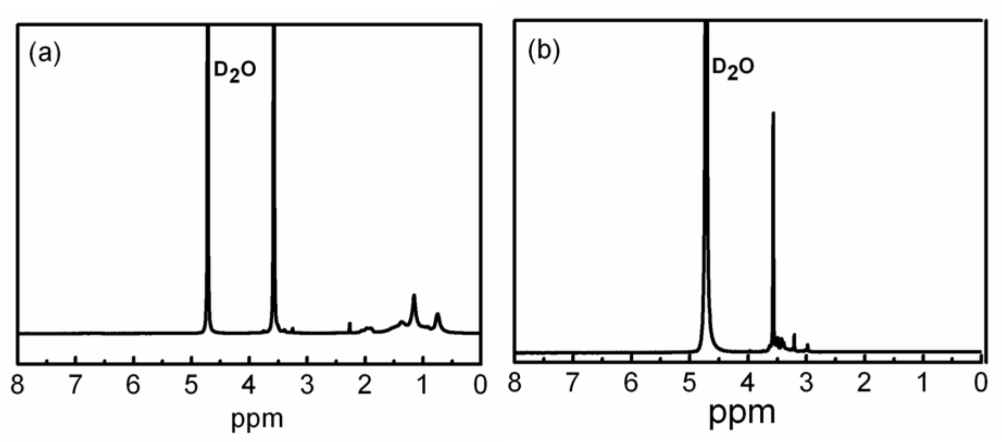

Figure S3. ^{1}H NMR spectra of GP1 nanocapsules recorded in D_2O before (a) and after (b) crosslinking treatment.