

Communication

Supporting Information: Degradable Polymer Stars Based on Tannic Acid Cores by ATRP

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1. UV/vis Spectra

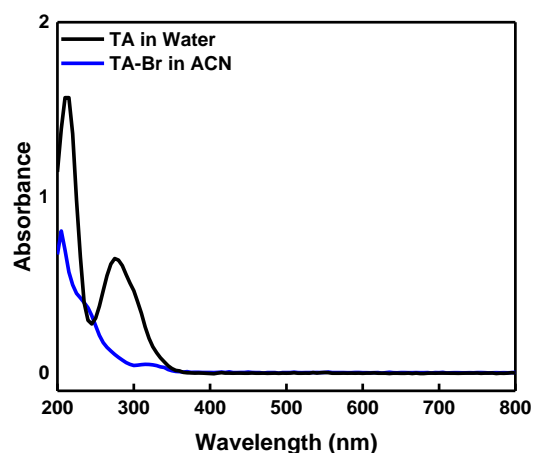
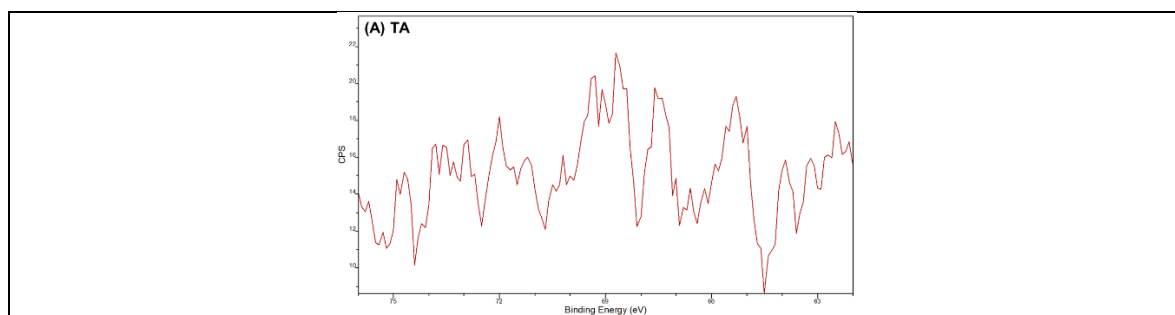


Figure S1. UV/vis spectra of tannic acid (TA) in water (black, 0.001 mg/mL) and TA-Br in acetonitrile (ACN) (blue, 0.001 mg/mL). Different solvents were used due to the chemical solubilities. TA is insoluble in ACN and TA-Br is insoluble in water.

2. XPS Br3d Scan



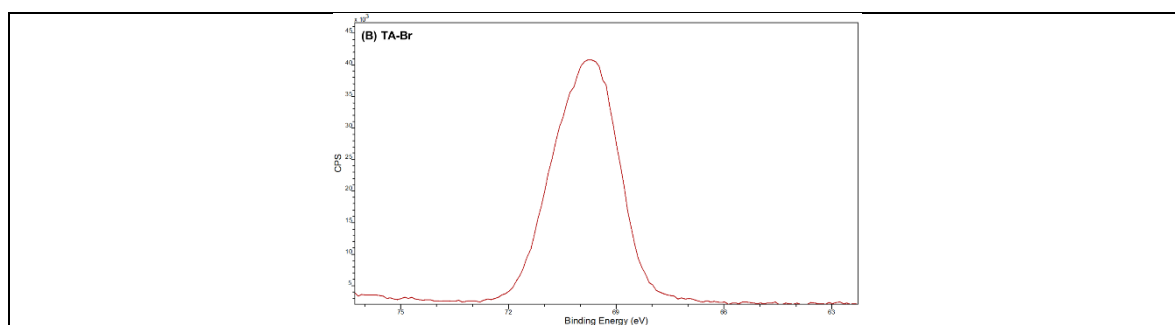


Figure S2. The high resolution XPS Br 3d spectra of (A) Tannic acid and (B) TA-Br.

3. Polymer Star Synthesis and Degradation

3.1. The polymer star synthesis

Table S1. The polymer stars prepared by growing either poly(methyl methacrylate) (PMMA) or P(OEO₃₀₀MA) arms by photo atom transfer radical polymerization (ATRP) (5.2 mW/cm²; λ = 365 nm).

| Entry ¹ | Core | Monomer | [M]/[Core]/[CuBr ₂]/[Me ₆ TREN] ¹ | DP _{target} /arm ² | Conv. (%) ³ |
|--------------------|---------|-----------------------|---|--|------------------------|
| 1 | TA-Br | MMA | 250/25/1/6 | 10 | 72 |
| 2 | TA-Br | MMA | 1250/25/1/6 | 50 | 50 |
| 3 | TP-iBBr | MMA | 2000/1/0.24/1.44 | 333 | 16 |
| 4 | TA-Br | OEO ₃₀₀ MA | 1500/25/1/6 | 60 | 43 |
| 5 | TA-Br | OEO ₃₀₀ MA | 5000/25/1/4 | 200 | 19 |

¹Molar equivalents; [M] = monomer; Concentration: [MMA] = 0.9M; [OEO₃₀₀MA] = 0.5M; ²Assuming 25 arms per star for TA-Br and 6 arms per star for TP-iBBr. ³Determined by ¹H NMR conversion of vinyl bonds.

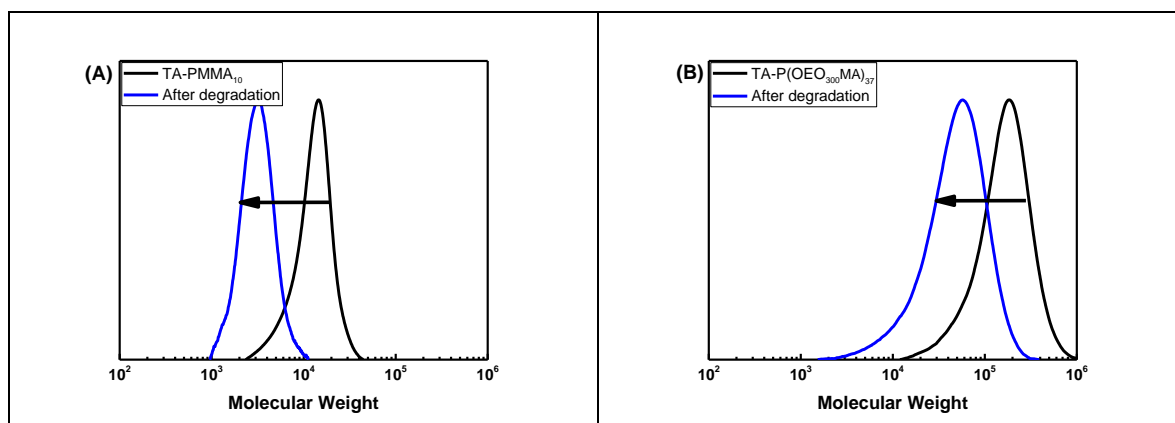
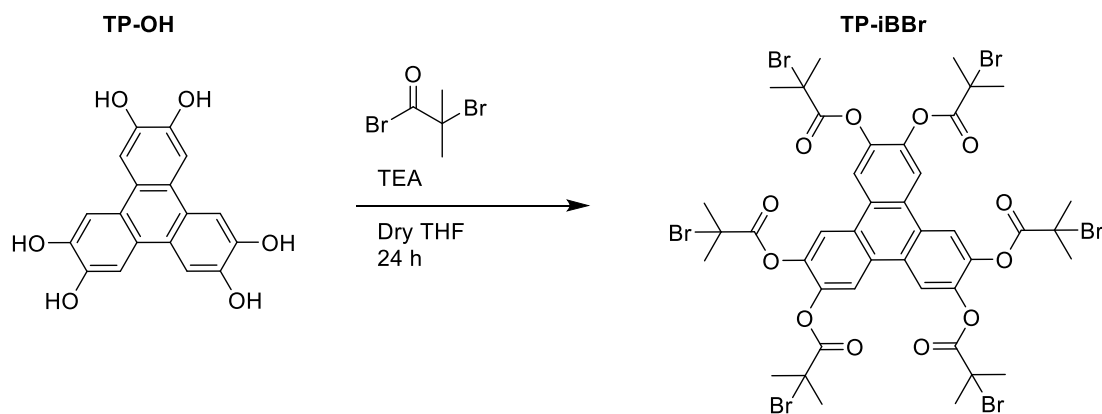


Figure S3. (A) The GPC traces of TA-PMMA₁₀ and (B) TA-P(OEO₃₀₀MA)₃₇ before (black) and after (blue) degradation.

3.2. TP-iBBr Synthesis

Scheme S1. The synthesis of TP-iBBr.



In a dry Schlenk flask (100 mL), TP-OH (1.2g, 3.70 mmol, 1 eq.) was dissolved dry THF (50 mL). TEA was added (4.3 mL, 30.8 mmol, 8.3 eq.) and the solution was cooled to 0°C in an ice bath. α -bromoisobutyryl bromide (3.58 mL, 30.0 mmol, 7.8 eq.) was added dropwise. Then the solution was removed from the ice bath and stirred at room temperature in the sealed flask overnight. The reaction mixture was gravity filtered and the solution was concentrated in vacuo. The solution was dissolved ether (200 mL), washed three times with NaHCO₃ saturated DI water solution (3x200 mL) and twice with distilled water (2x50 mL). The organic phase was concentrated in vacuo and dissolved in a minimum of ethyl acetate. The product (TP-iBBr) was obtained by precipitate in hexane and subsequent centrifugation (2.6 g, 2.13 mmol, molar mass = 1218.21 g/mol, yield = 58 %). ¹H-NMR: (500 MHz, CDCl₃) δ 8.31 (s, 6H), 2.16 (s, 36H).

3.3. Degradation followed by GPC and UV/vis

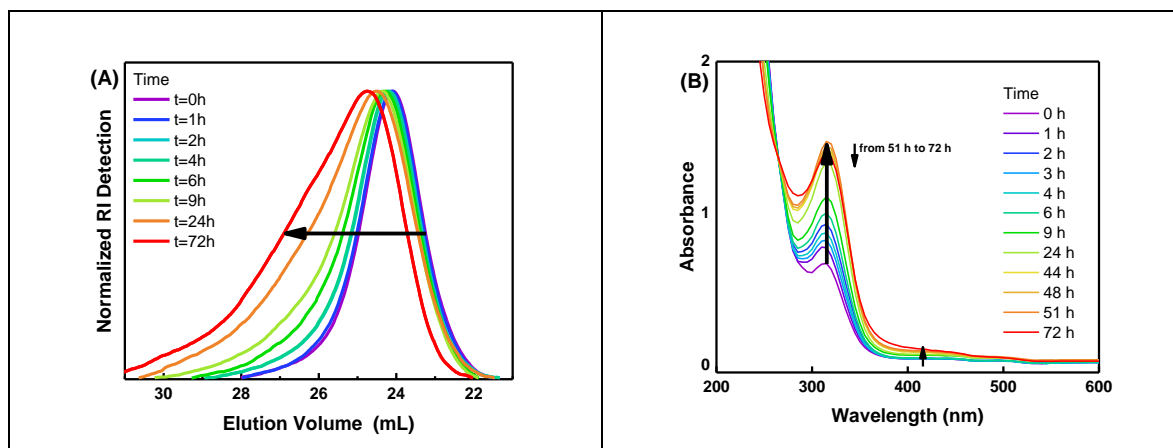


Figure S4. (A) The GPC traces of TA-P(OEO₃₀₀MA)₂₅ degradation in sat. NaHCO₃/MeOH. (B) The UV/vis spectra over time. The solution prepared was 5 mg/mL TA-P(OEO₃₀₀MA)₂₅ (total solution volume 15 mL). This solution was more concentrated in order to remove 1 mL samples at each time interval and have enough polymer for GPC.

4. Cytotoxicity Assays

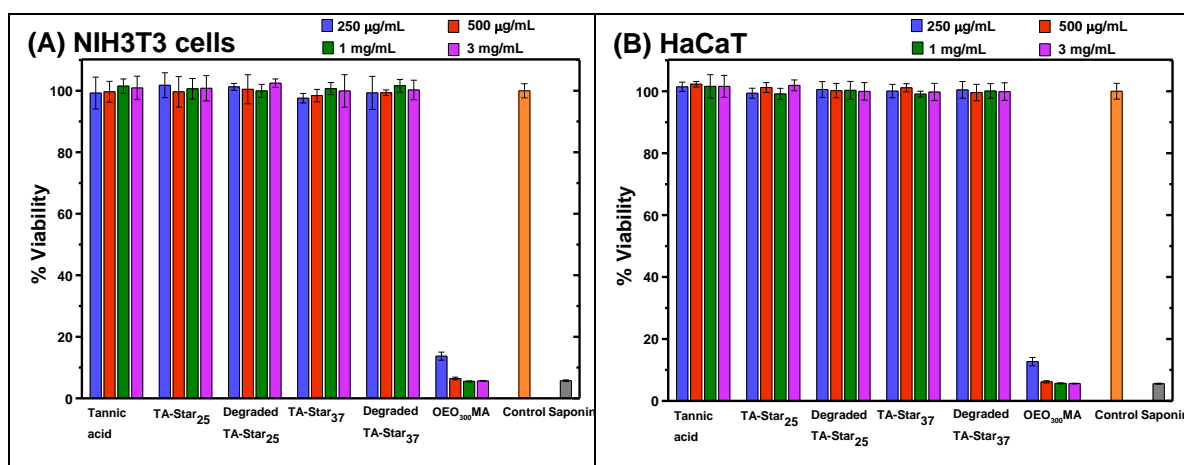


Figure S5. The percent viability of (A) NIH3T3 cells and (B) HaCaT cells, after 72 h of TA-P(OEO₃₀₀MA) polymer stars, samples after degradation, and OEO₃₀₀MA monomer at four concentrations from 250µg-3 mg/mL. Positive (orange) and negative controls (Saponin, grey) are also shown.