# Electronic Supplementary Information for

## With Polymer Photoclicks to Fluorescent Microspheres

Jordan P. Hooker,[a] Laura Delafresnaye,[a] Leonie Barner*[a] and Christopher Barner-Kowollik*[ab]

[a] School of Chemistry Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia. Email: christopher.barnerkowollik@qut.edu.au; leonie.barner@qut.edu.au

[b] Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76131 Karlsruhe, Germany.

**Contents**

## 1. Materials

All materials were reagent grade and used as received, unless stated otherwise. Styrene and chloromethylstyrene were deinhibited by passing over a column of activated basic alumina (*Ajax*) immediately prior to use. Acrylic acid, *p*-anisidine, (1-bromoethyl)benzene, Copper powder, 4-methylbenzenesulfonohydrazide, 2,2,6,6-tetramethyl-1- piperidinyloxy (TEMPO), *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA), pyridine and styrene were purchased from *Sigma Aldrich*. Cesium carbonate ($Cs_2CO_3$), chloromethylstyrene (CMS), 4-formylbenzoic acid, hydrochloric acid (32%) and sodium nitrite were purchased from *Thermo Fisher Scientific*. Acetonitrile (ACN), dichloromethane (DCM), dimethylformamide (DMF), ethanol, ethyl acetate, methanol, tetrahydrofuran (THF) and toluene were purchased from *Thermo Fisher Scientific*. Chloroform-$d_1$ and dimethylsulfoxide-$d_6$ were purchased from *Sigma-Aldrich*.

## 2. Methods

**Particle Synthesis:**

For a typical reaction, a ***P2α*** P(St-*co*-Tet) solution in ACN and a ***P3*** P(St-*co*-Acr) solution in ACN were combined and diluted to desired concentrations in either ACN or a combination of ACN:THF. The reaction mixture was then filtered through a 0.22 µm PTFE syringe filter into a silanized crimp vial and sealed to prevent evaporation of the solvent. Reactions were well-mixed and shaken at 100 rpm or rolled at 2 rpm* and irradiated (λ = 300 nm) for 30 or 120 min, with concentrations above 1 mg $mL^{-1}$ having a longer irradiation time due to lower penetration depth of the incident light. The crude reaction mixture was then centrifuged at 5000 rpm for 10 min, and the sediment dispersed twice in THF followed by centrifugation to yield the isolated microspheres.

* Refer to Section **3** for photoreactor setups (Fig. S11-12).

**Particle Degradation:**

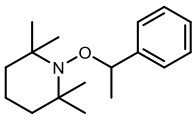
For particle degradation, 5 mg of microspheres were dispersed in a solution of 0.1 M NaOH in THF (5 mL). At the specified time points, samples for SEM analysis were drop cast directly onto an aluminium stub. For fluorescence analysis, samples were centrifuged for 10 min at 5000 rpm to sediment any remaining particles, and the clear upper solution analysed by fluorescence spectroscopy.

**Particle Encapsulation:**

4-bromothiophenol (10 mg) was added to a solution of solvent-swollen microspheres (10 mg) in THF (5 mL) and shaken at 100 rpm. After 1 h, the solution was centrifuged at 5000 rpm for 10 min, then washed with ACN (5 mL) and then 4 times with THF (5 mL) to remove material adsorbed to the surface. After drying for 1 h, the microspheres were analyzed via XPS analysis to confirm the presence of 4-bromothiophenol.

**2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (1):**

**1** was synthesised according to a modified procedure from the literature.[1]



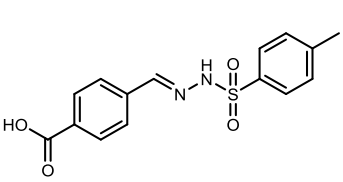
(1-bromoethyl)benzene (2.00 mL, 14.7 mmol, 1 eq) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (2.562 g, 16.40 mmol, 1.1 eq) were dissolved in dry acetonitrile (10 mL). Copper powder (0.469 g, 7.38 mmol, 0.5 eq) was added, and the solution was degassed by bubbling with argon for 10 min. *N,N,N′,N″,N‴*-Pentamethyldiethylenetriamine (PMDETA) (1.85 mL, 8.9 mmol, 0.6 eq) was added by syringe. The reaction was stirred overnight at room temperature. The product was isolated by column chromatography on basic aluminium oxide with toluene as eluent. Solvent was removed *in vacuo*, yielding **1** (3.312 g, 87 %) as a white, crystalline solid.

**$^{1}$H-NMR** ($CDCl_3$, 600 MHz) δ = 7.34-7.30 (4H, m, CH), 7.24-7.22 (1H, m, CH), 4.79 (1H, q, $^{3}J_{HH}$ = 6.7 Hz, CH), 1.50-1.04 (18H, m, $CH_3$/$CH_2$), 0.67 ppm (3H, s, $CH_3$).

**$^{13}$C-NMR** ($CDCl_3$, 150 MHz) δ = 146.0, 128.1, 126.9, 126.7, 83.3, 59.8, 40.5, 34.6, 34.3, 23.7, 20.5, 17.4 ppm.

**4-[[2-[(4-Methylphenyl)sulfonyl]hydrazinylidene]methyl]benzoic acid (2):**

**2** was synthesised according to a modified procedure from the literature.[2]



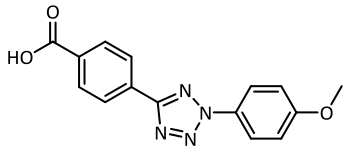
A mixture of 4-formylbenzoic acid (9.260 g, 61.682 mmol, 1 eq) and 4-methylbenzenesulfonohydrazide (11.486 g, 61.674 mmol, 1 eq) in ethanol (250 mL) was heated to reflux for 30 min. The reaction mixture was diluted with water (250 mL) and the precipitate collected by vacuum filtration. The precipitate was washed with aqueous ethanol (1:1, 100 mL) and dried under vacuum, yielding **2** as a fine white solid (18.525 g, 94 %).

**$^{1}$H-NMR** (DMSO-$d_6$, 600 MHz) δ = 13.09 (1H, s, broad, COOH), 11.69 (1H, s, broad, NH), 7.96 (1H, s, CH), 7.94 (2H, d, $^{3}J_{HH}$ = 8.4 Hz, 2 × CH), 7.77 (2H, d, $^{3}J_{HH}$ = 8.3 Hz, 2 × CH), 7.67 (2H, d, $^{3}J_{HH}$ = 8.4 Hz, 2 × CH), 7.40 (2H, d, $^{3}J_{HH}$ = 8.2 Hz, 2 × CH), 2.34 ppm (3H, s, $CH_3$).

**$^{13}$C-NMR** (DMSO-$d_6$, 150 MHz) δ = 166.8 (C), 145.7 (CH), 143.6 (C), 137.6 (C), 136.1 (C), 131.7 (C), 129.8 (4 × CH), 127.2 (2 × CH), 126.8 (2 × CH), 21.0 ppm (CH3).

**4-(2-(4-methoxyphenyl)-2H-tetrazol-5-yl)benzoic acid (3):**

**3** was synthesised according to a modified procedure from the literature.[2]

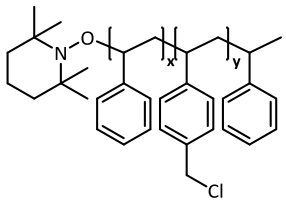


*p*-Anisidine (4.1353 g, 33.577 mmol, 1 eq.) was dissolved in a mixture of concentrated HCl (8.5 mL), $H_2O$ (27 mL) and ethanol (27 mL) and cooled to 0 °C. A cooled solution of $NaNO_2$ (2.3534 g, 34.112 mmol, 1.016 eq.) in $H_2O$ (13.5 mL) was added dropwise and stirred for 10 min at 0 °C. The in situ generated diazonium salt solution was added dropwise to a solution of **2** (10.98 g, 34.49 mmol, 1.03 eq.) in pyridine (200 mL) at -10 °C – -5 °C. After complete addition, the solution was stirred at 0 °C for 30 min and at ambient temperature overnight. The turbid solution was poured into HCl solution (10% aq, 500 mL) and the precipitate filtered off and washed with acetonitrile (200 mL) and toluene (200 mL). After drying under vacuum, **3** was yielded as a beige-pink solid (5.68 g, 57 %).

**$^1$H-NMR** (DMSO-$d_6$, 600 MHz) δ = 13.23 (1H, s, broad, OH), 8.24 (2H, d, $^3J_{HH}$ = 8.4 Hz, Ar CH) 8.13 (2H, d, $^3J_{HH}$ = 8.4 Hz, Ar CH) 8.05 (2H, d, $^3J_{HH}$ = 9.1 Hz, ArCH), 7.20 (2H, d, $^3J_{HH}$ = 8.4 Hz, Ar CH), 3.86 ppm (3H, s, $OCH_3$).

**$^{13}$C-NMR** (DMSO-$d_6$, 150 MHz) δ = 166.7, 163.5, 160.5, 132.6, 130.2, 129.5, 126.7, 121.7, 115.1, 55.7 ppm.

***Poly(styrene-co-chloromethylstyrene) (P1a):***



Initiator **1** (0.5195 g) was added to a schlenk tube and dissolved in styrene (7 mL) and chloromethylstyrene (2 mL). The reaction mixture was degassed by bubbling with argon for 30 min, then heated to 120 °C. After 60 min the reaction was stopped by cooling the flask in liquid nitrogen. The crude mixture was dissolved in a small amount of THF (2 mL) and added dropwise to a solution of cold methanol. The precipitate was collected by filtration and dried under vacuum, yielding the product (**P1a**) as a white solid (1.2461 g).

**$^1$H-NMR** ($CDCl_3$, 600 MHz) δ = 7.30 – 6.20 (m, ArH), 4.65 – 4.30 (s, br, $CH_2Cl$), 2.50 – 0.84 ppm (m, aliphatic H).

**SEC (PS cal.)**: 1350 g.mol$^{-1}$, *Đ* 1.1.

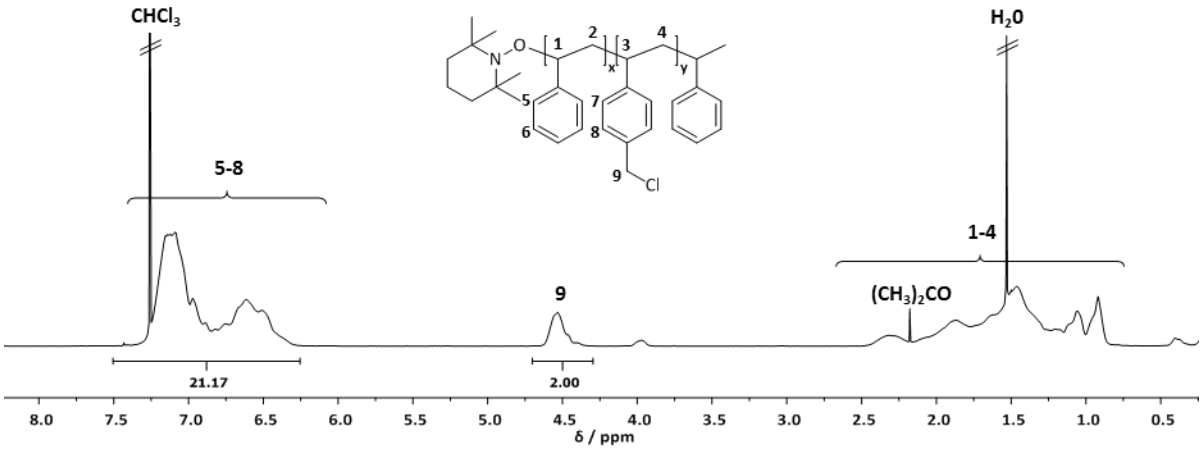



**Fig. S1**: $^{1}$H-NMR spectrum of **P1a** in chloroform-$d_1$

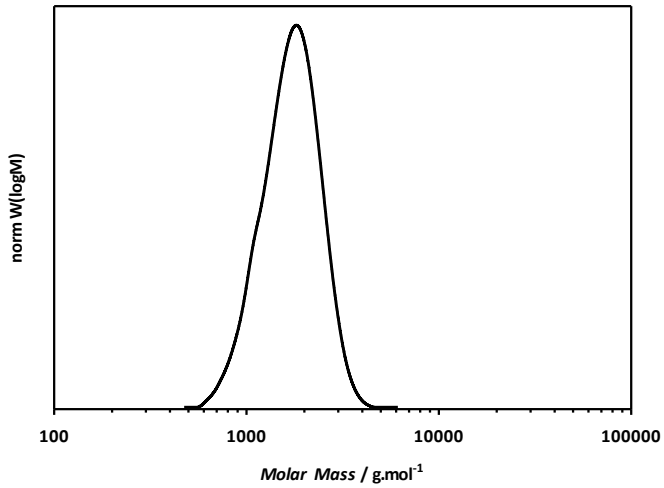
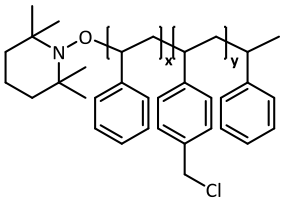



**Fig. S2**: SEC trace of **P1a** in THF using polystyrene calibration.

***Poly(styrene-co-chloromethylstyrene) (P1b):***



Initiator **1** (0.5232 g) was added to a schlenk tube and dissolved in styrene (6 mL) and chloromethylstyrene (3 mL). The reaction mixture was degassed by bubbling with argon for 30 min, then heated at 120 °C. After 120 min the reaction was stopped by cooling the flask with liquid nitrogen. The crude mixture was dissolved in a small amount of THF (2 mL) and added dropwise to a solution of cold methanol. The precipitate was collected by filtration and dried under vacuum, yielding the product (**P1b**) as white solid (1.638 g).

**$^{1}$H-NMR** ($CDCl_3$, 600 MHz) δ = 7.30 – 6.20 (m, ArH), 4.65 – 4.30 (s, br, $CH_2Cl$), 2.50 – 0.84 ppm (m, aliphatic H).

**SEC (PS cal.)**: 2050 g.mol$^{-1}$, *Đ* 1.2.

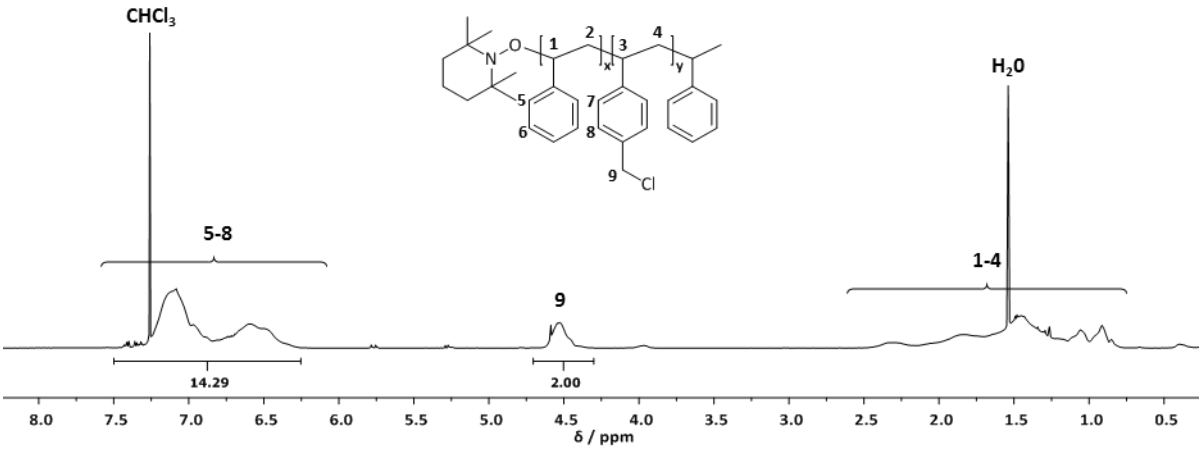



**Fig. S3**: $^{1}$H-NMR spectrum of **P1b** in chloroform-$d_1$

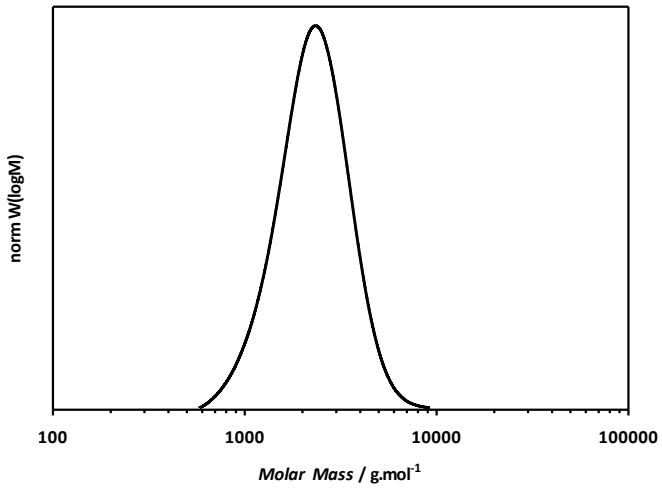
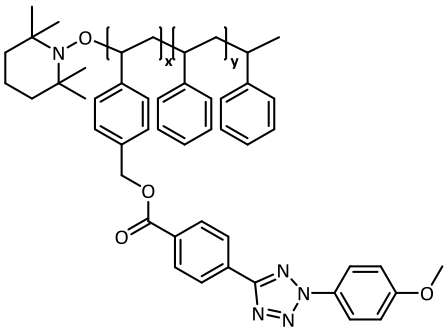



**Fig. S4**: SEC trace of **P1b** in THF using polystyrene calibration.

***Poly(styrene-co-Tetrazole) (P2a):***



Poly(styrene-*co*-chloromethylstyrene) (**P1a**) (0.2257 g, 1 eq)**,** **5** (0.1512 g, 1.05 eq) and $Cs_2CO_3$ (0.2705, 2 eq) were dissolved in DMF (30 mL), and stirred at 40 °C for 96 h. DMF was removed under reduced pressure and the reaction mixture diluted with DCM (50 mL), washed twice with water (50 mL), and then twice with brine (50 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure. The residue was dissolved in THF and precipitated into cold methanol. The precipitate was filtered under vacuum and washed with cold methanol, yielding the product (**P2a**) as a pale pink solid (0.2342 g).

**$^1$H-NMR** ($CDCl_3$, 600 MHz) δ = 8.35 – 7.85 (m, br, TetArH), 7.30 – 6.20 (m, ArH), 5.43 – 5.00 (s, br, $CH_2O$), 3.90 – 3.70 (s, br, MeO), 2.50 – 0.84 ppm (m, aliphatic H).

**SEC (PS cal.)**: 1900 g.mol$^{-1}$, *Đ* 1.1.

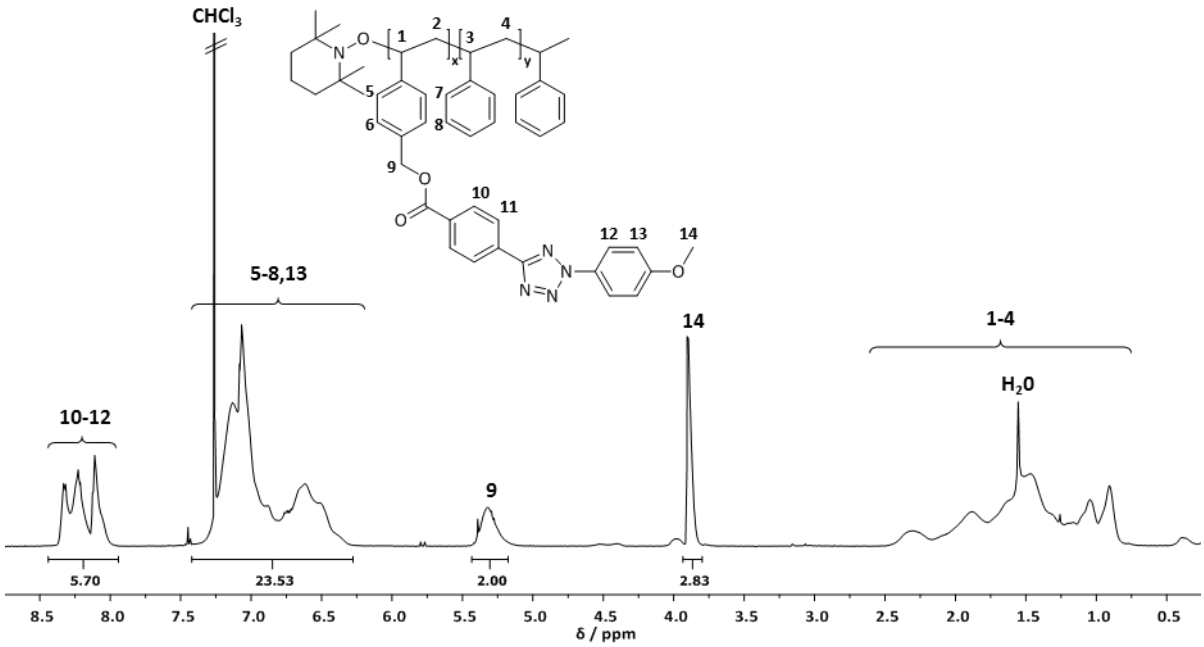



**Fig. S5**: $^1$H-NMR spectrum of **P2a** in chloroform-$d_1$

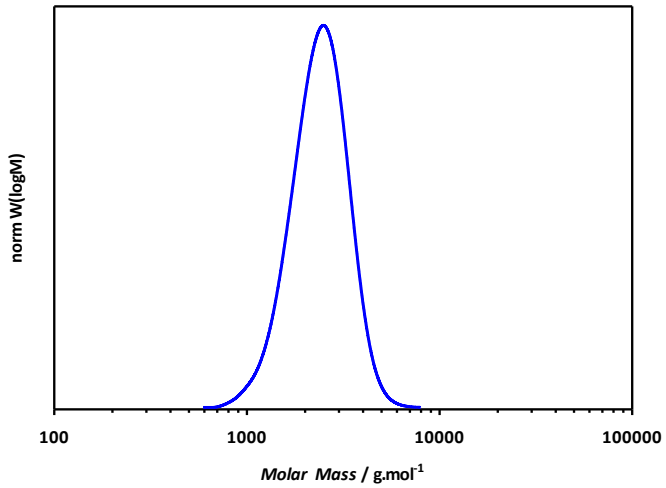
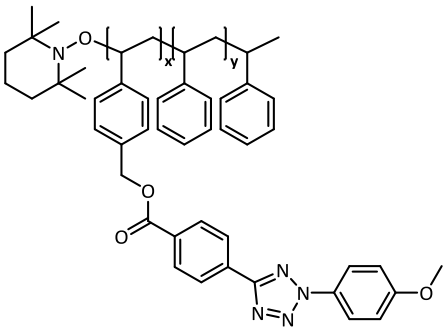



**Fig. S6**: SEC trace of **P2a** in THF using polystyrene calibration.

***Poly(styrene-co-Tetrazole) (P2b):***



Poly(styrene-*co*-chloromethylstyrene) ($M_n$: 1850 g mol$^{-1}$, Đ: 1.1) (0.2011 g, 1 eq)**, 5** (0.1410 g, 1.05 eq) and $Cs_2CO_3$ (0.2900 g, 2 eq) were dissolved in DMF (30 mL), and stirred at 40 °C for 96 h. DMF was removed under reduced pressure and the reaction mixture diluted with DCM (50 mL), washed twice with water (50 mL), and then twice with brine (50 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure. The residue was dissolved in THF and precipitated into cold methanol. The precipitate was filtered under vacuum and washed with cold methanol, yielding the product (**P2b**) as a pale pink solid (0.2084 g).

**$^1$H-NMR** ($CDCl_3$, 600 MHz) δ = 8.35 – 7.85 (m, br, TetArH), 7.30 – 6.20 (m, ArH), 5.43 – 5.00 (s, br, $CH_2O$), 3.90 – 3.70 (s, br, MeO), 2.50 – 0.84 ppm (m, aliphatic H).

**SEC (PS cal.)**: 2650 g.mol$^{-1}$, *Đ* 1.1.

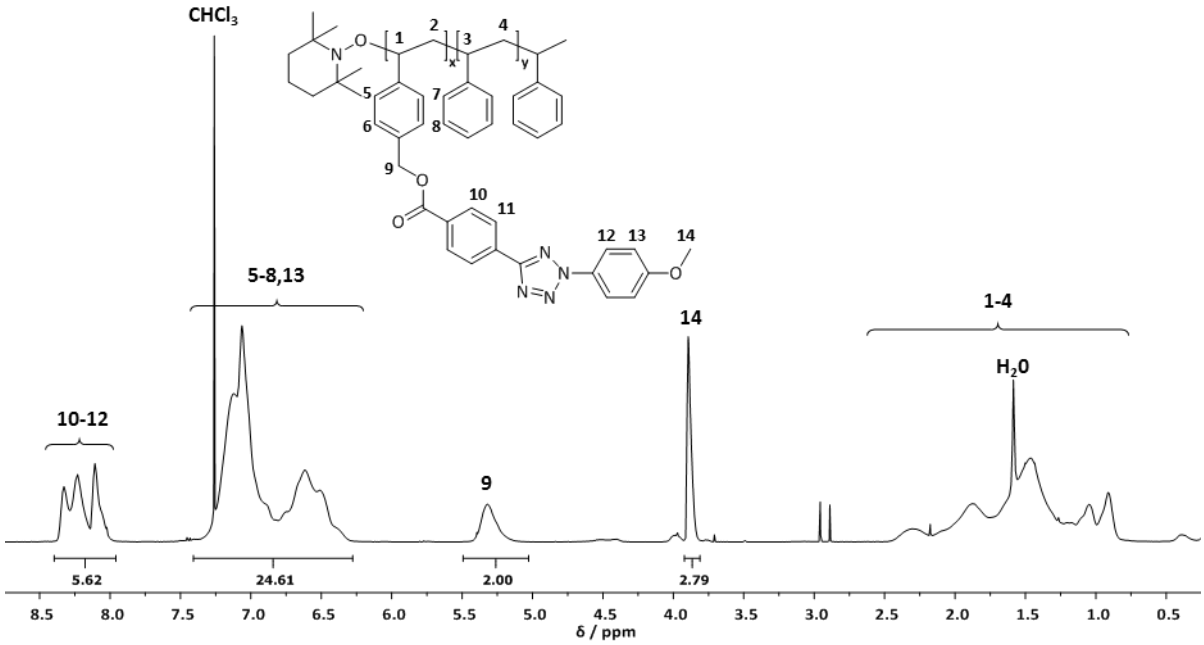



**Fig. S7**: $^1$H-NMR spectrum of **P2b** in chloroform-$d_1$

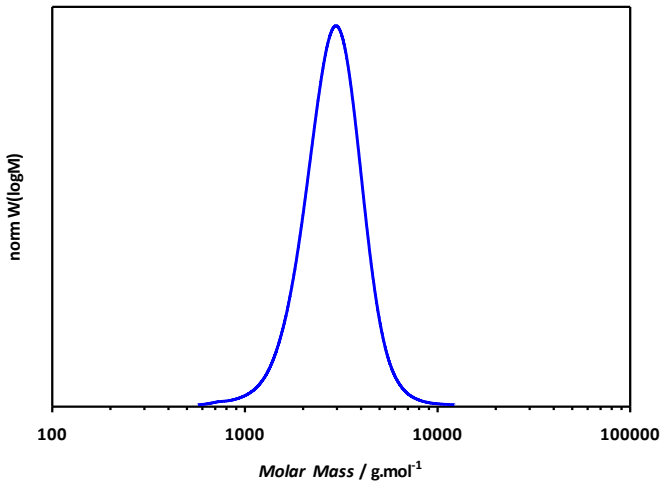
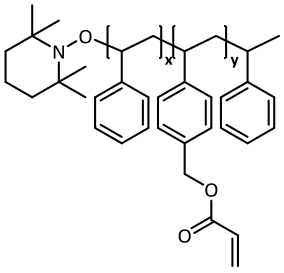



**Fig. S8**: SEC trace of **P2b** in THF using polystyrene calibration.

***Poly(styrene-co-Acrylate) (P3b):***



Poly(styrene-*co*-chloromethylstyrene) (**P1b**) (0.5341 g, 1 eq), acrylic acid (0.48 mL, 5 eq) and $K_2CO_3$ (0.9272 g, 2.5 eq) were dissolved in DMF (50 mL), and stirred at room temperature for 72 h. Subsequently, DMF was removed under reduced pressure and the reaction mixture diluted with ethyl acetate (50 mL), washed twice with water (50 mL) and then twice with brine (50 mL). The organic phase was dried with $MgSO_4$, and the solvent removed under reduced pressure. The residue was dissolved in THF and precipitated into cold methanol. The precipitate was filtered under vacuum and washed with cold methanol, yielding the product **P3b** as a white solid (0.5070 g).

**$^1$H-NMR** ($CDCl_3$, 600 MHz) δ = 7.30 – 6.30 (m, ArH), 6.45 (s, br, C=CH), 6.18 (s, br, CH=C), 5.85 (s, br, C=CH), 5.24 – 5.00 (s, br, $CH_2O$), 2.50 – 0.84 ppm (m, aliphatic H).

**SEC (PS cal.)**: 2500 g.mol$^{-1}$, *Đ* 1.1.

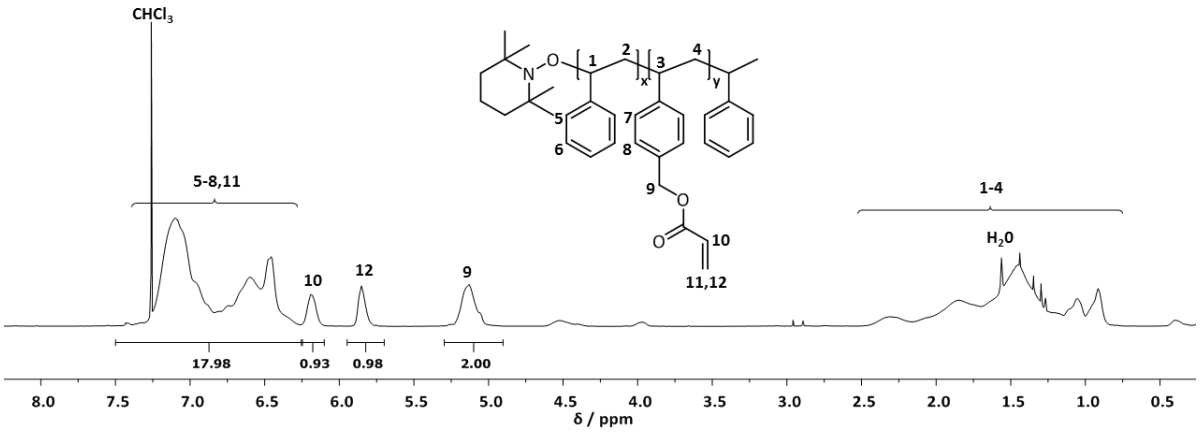



**Fig. S9**: $^{1}$H-NMR spectrum of **P3b** in chloroform-$d_1$.

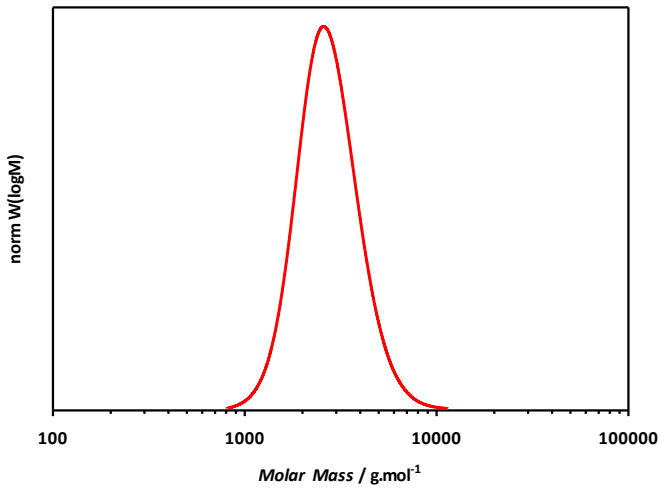



**Fig. S10**: SEC trace of **P3b** in THF using polystyrene calibration.

***Table S1**: XPS analysis of the premade polymer before and after functionalisation.*[a]

| | | C *1s* (at%) | O *1s* (at%) | N *1s* (at%) | Cl *2p* (at%) |
|---|---|---|---|---|---|
| ***P1a*** | ***P(St-co-CMS)*** | 95.54 ± 0.20 | 1.55 ± 0.16 | 0.95 ± 0.07 | 1.95 ± 0.12 |
| ***P2a*** | ***P(St-co-Tet)*** | 91.40 ± 0.41 | 4.29 ± 0.19 | 4.25 ± 0.23 | 0.06 ± 0.01 |
| ***P1b*** | ***P(St-co-CMS)*** | 94.16 ± 0.13 | 1.71 ± 0.19 | 0.68 ± 0.11 | 3.46 ± 0.04 |
| ***P3b*** | ***P(St-co-Acr)*** | 93.92 ± 0.19 | 5.16 ± 0.15 | 0.69 ± 0.13 | 0.24 ± 0.03 |

[a] Analysis performed at room temperature on carbon tape. Average values and standard deviation of three different locations.

## 3. Characterisation and Instrumentation

*Particle Synthesis 'Photoreactor':* Reactions were performed on either a *Heidolph* Vibramax 100 (Fig. S11) at 100 rpm, or a *ThermoScientific* Bottle Roller at 2 rpm (Fig. S12). Irradiation was done using 2 x 8W UVB lamps with an emission wavelength centred on 300 nm. Irradiation times were either 30 min or 2 h, with concentrations above 1 mg $mL^{-1}$ having a longer irradiation time due to lower penetration depth of the incident light. The bottle roller additionally ensured the uniform, mild agitation required at higher concentrations (above 1 mg $mL^{-1}$).

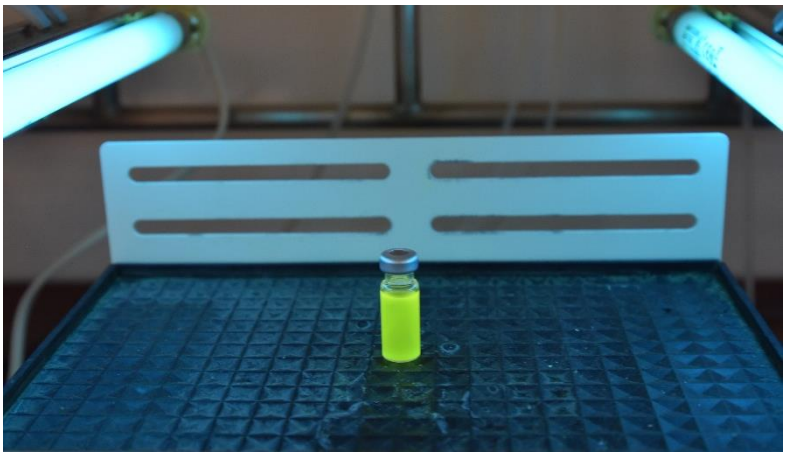


**Fig. S11***:* Image of particle synthesis setup using a platform shaker, consisting of a vial placed on a shaker at 100 rpm, irradiated from each side by two 8W UVB lamps (λ = 300 nm).

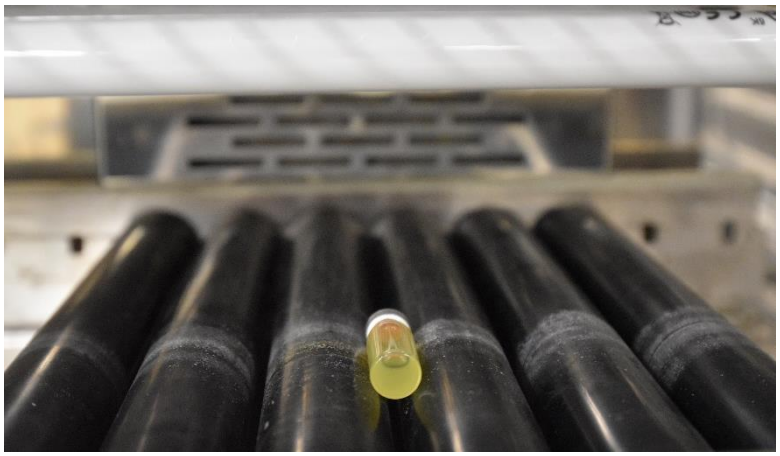


**Fig. S12**: Image of particle synthesis setup using a bottle roller, consisting of a vial placed on a roller at 2 rpm, irradiated from above by one 8W UVB lamp (λ = 300 nm).

*Nuclear Magnetic Resonance (NMR) Spectrometry:* $^{1}H$ and $^{13}C$-NMR spectra were recorded on a *Bruker* System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient ($^{1}H$: 600.13 MHz, $^{13}C$ 150.90 MHz). The δ-scale was normalized relative to the solvent signal of $CHCl_3$ or DMSO for $^{1}H$ spectra and for $^{13}C$ spectra on the middle signal of $CHCl_3$ triplet or the DMSO quintet. The multiplicities were reported using the following abbreviations: s for singlet, d for doublet, t for triplet, m for multiplet and br for broad signal.

*THF Size Exclusion Chromatography (SEC):* The SEC measurements were conducted on a *PSS* SECurity$^2$ system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8x150 mm 5 µm Precolumn, 8x300 mm 5 µm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, was used as eluent at a flow rate of 1 $mL \cdot min^{-1}$. Narrow disperse linear poly(styrene) ($M_n$: 266 $g \cdot mol^{-1}$ to $2.52x10^6$ $g \cdot mol^{-1}$) and poly(methyl methacrylate) ($M_n$: 202 $g \cdot mol^{-1}$ to $2.2x10^6$ $g \cdot mol^{-1}$) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analyses were performed in *PSS* WinGPC UniChrom software (version 8.2).

*Dynamic Light Scattering (DLS):* Particle sizes (the average diameters and size distributions) were determined using a Malvern Zetaplus particle size analyzer (laser, 35mW, λ = 632 nm, angle = 90 °). Samples were prepared highly diluted in THF for DLS analysis, equilibrated for 30 seconds, and analyses run in triplicate. The count rate was kept in between 100 and 500 kcps.

*Fluorescence Spectroscopy:* The fluorescence intensities were measured using a Cary Eclipse Fluorescence Spectrophotometer from *Agilent Technologies*. Voltage was set to medium, with an excitation wavelength of 400 nm. Samples were prepared in THF and measured at ambient temperature in *Helma Analytics* quartz high precision cells with a path length of 10 mm. For kinetic analysis, 10 µL of the crude reaction mixture was diluted to 2.5 mL. For analysis of isolated particles, a concentration of 1 mg $mL^{-1}$ was used.

*Centrifuge:* The particles were isolated by centrifugation using a Sigma 3-16L centrifuge, at 5000 rpm for 10 minutes.

*Optical Microscopy:* Fluorescence images were captured using a Nikon A1R confocal microscope using a channel with an excitation peak of 488 nm. Analysis was done using NIS AR Elements. Samples were prepared by dispersing in THF and drop casting onto a glass slide.

*Scanning Electron Microscopy:* SEM images were captured using a Zeiss Sigma VP Field emission SEM at 0.7 kV using an in-lens SE detector, or a Tescan MIRA3 SEM at 2 kV using an in-lens SE detector with beam-deceleration mode. Samples were prepared by dispersing the particles in THF or ACN and drop casting onto a silicon wafer. Samples were coated with a 10 nm layer or either platinum or gold. Analysis was done in ImageJ, with particle sizing and dispersity calculations based on counting a minimum of 100 particles, using the following equations:

$$D_n = \frac{\sum N_i D_i}{\sum N_i}$$

$$D_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3}$$

Where $D_n$ is the number-average diameter, $D_w$ is the weight-average diameter, $N_i$ is the number of particles measured, and $D_i$ is the diameter of the measured particle. The dispersity Đ can then be calculated as

$$Đ = \frac{D_w}{D_n}$$

*X-ray Photoelectron Spectroscopy (XPS):* XPS samples were prepared using the dry particles after purification and removal of the solvent. The powder-like material was subsequently casted on carbon tape. X-Ray Photoelectron Spectroscopy analysis was performed under incident conditions, the X-ray penetration depth being lower than 5 nm (ultrathin layer method). A Kratos Axis Supra photoelectron spectrometer was used with a monochromatic incident radiation (A1 X-rays: HT - 15.1 kV; Emission current - 15 mA). Base pressure in the analysis chamber was 1.0 $10^{-8}$ Torr. Survey (wide) scans were carried out over 1200-0 eV binding energy range with 1.0 eV steps. Narrow higher resolution scans

were run with 0.1 eV steps and 60 s sweep time (5 sweeps). The experimental data were analysed using the software CasaXPS.

## 4. Analysis of Copolymer Functionality and Composition

**Calculation of monomer ratios:**

The percentage of functional monomer in each copolymers was calculated from the $^1$H-NMR spectra using the ratio of the $CH_2$-group and compared to the total aromatic protons and additional protons from either the tetrazole or acrylate functionality. Overlap of the aromatic styrene-H peaks makes selecting single peaks for comparison not possible. Contribution to the aromatic integral from the initiator is considered to be negligible.

Chemical shifts (δ) used in calculations:

∫($CH_2$) **P1a/b** δ ($^1$H) = 4.3 – 4.7

∫($CH_2$) **P2a/b** δ ($^1$H) = 5.1 – 5.5

∫($CH_2$) **P3** δ ($^1$H) = 4.9 – 5.3

∫(Ph-H) **P1/2/3** δ ($^1$H) = 6.25 – 7.5

∫(Tet-H) **P2a/b** δ ($^1$H) = (3.8 – 3.95) + (7.95 – 8.4)

∫(Acr-H) **P3** δ ($^1$H) = (5.7 – 5.95) + (6.1 – 6.25)

**P1a:**

$$\frac{5}{2 \cdot \frac{\int(Ph-H)}{\int(CH_2)} + 1}$$

$$\frac{5}{2 \cdot \frac{21.17}{2} + 1} = \mathbf{22.6}\ \%$$

**P1b:**

$$\frac{5}{2 \cdot \frac{\int(Ph-H)}{\int(CH_2)} + 1}$$

$$\frac{5}{2 \cdot \frac{14.29}{2} + 1} = \mathbf{32.7}\ \%$$

**P2a:**

$$\frac{5}{2 \cdot \frac{\int(Ph-H)+\int(Tet-H)}{\int(CH_2)} - 10}$$

$$\frac{5}{2 \cdot \frac{23.53+(5.70+2.83)}{2} - 10} = \mathbf{22.7}\ \%$$

**P2b:**

$$\frac{5}{2 \cdot \frac{\int(Ph-H)+\int(Tet-H)}{\int(CH_2)} - 10}$$

$$\frac{5}{2 \cdot \frac{24.61+(5.62+2.79)}{2} - 10} = \mathbf{21.7}\ \%$$

**P3:**

$$\frac{5}{2 \cdot \frac{\int(Ph-H)+\int(Acr-H)}{\int(CH_2)} - 2}$$

$$\frac{5}{2 \cdot \frac{17.98+(0.93+0.98)}{2} - 2} = \mathbf{27.9}\ \%$$

**Calculation of functional monomer per polymer chain:**

Using the percentages obtained above from the $^1$H-NMR spectra and the $\boldsymbol{M}_\mathbf{n}$ determined by SEC, the average number of units of functional monomer per polymer chain were approximated as follows:

**P1a:**

$$n(CMS) = n(monomers) \cdot X(CMS)$$

Where $n(monomers)$ is the average number of monomers per polymer chain.

$X(CMS)$ is the fraction of CMS in the copolymer

$$n(monomers) = \frac{M_n(Polymer) - M(NMPgroup)}{M_{Average}(monomer)}$$

Where $M_n(polymer)$ is the number-average molar mass of the copolymer determined by SEC.

*M(NMPgroup)* is the molar mass of the NMP initiator present in each polymer chain.

$M_{Average}(monomer)$ is the combined average monomer mass:

$$M_{Average} = X(CMS) \cdot M(CMS) + X(Styrene) \cdot M(Styrene)$$

Where *M(CMS)* is the molar mass of CMS.

*X(Styrene)* is the fraction of Styrene in the copolymer.

*M(Styrene)* is the molar mass of Styrene.

Combining for the number of CMS monomer units ($n(CMS)$):

$$n(CMS) = \frac{M_n(Polymer) - M(NMPgroup)}{X(CMS) \cdot M(CMS) + X(Styrene) \cdot M(Styrene)} \cdot X(CMS)$$

$$= \left( \frac{1350\ g.mol^{-1} - 261\ g.mol^{-1}}{0.226 \cdot 152\ g.mol^{-1} + 0.774 \cdot 104\ g.mol^{-1}} \right) \cdot 0.226 = 2$$

$$n(Styrene) = \frac{M_n(Polymer) - M(NMPgroup)}{X(CMS) \cdot M(CMS) + X(Styrene) \cdot M(Styrene)} \cdot X(Styrene)$$

$$= \left( \frac{1350\ g.mol^{-1} - 261\ g.mol^{-1}}{0.226 \cdot 152\ g.mol^{-1} + 0.774 \cdot 104\ g.mol^{-1}} \right) \cdot 0.774 = 7$$

**P1b**:

$$n(CMS) = \frac{M_n(Polymer) - M(NMPgroup)}{X(CMS) \cdot M(CMS) + X(Styrene) \cdot M(Styrene)} \cdot X(CMS)$$

$$= \left( \frac{2050\ g.mol^{-1} - 261\ g.mol^{-1}}{0.327 \cdot 152\ g.mol^{-1} + 0.673 \cdot 104\ g.mol^{-1}} \right) \cdot 0.327 = 5$$

$$n(Styrene) = \frac{M_n(Polymer) - M(NMPgroup)}{X(CMS) \cdot M(CMS) + X(Styrene) \cdot M(Styrene)} \cdot X(Styrene)$$

$$= \left( \frac{1850\ g.mol^{-1} - 261\ g.mol^{-1}}{0.327 \cdot 152\ g.mol^{-1} + 0.673 \cdot 104\ g.mol^{-1}} \right) \cdot 0.673 = 10$$

**P2a:**

$$n(Tet) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Tet) \cdot M(Tet) + X(Styrene) \cdot M(Styrene)} \cdot X(Tet)$$

$$= \left( \frac{1900\ g.mol^{-1} - 261\ g.mol^{-1}}{0.227 \cdot 412\ g.mol^{-1} + 0.773 \cdot 104\ g.mol^{-1}} \right) \cdot 0.227 = 2$$

$$n(Styrene) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Tet) \cdot M(Tet) + X(Styrene) \cdot M(Styrene)} \cdot X(Styrene)$$

$$= \left( \frac{1900\ g.mol^{-1} - 261\ g.mol^{-1}}{0.227 \cdot 412\ g.mol^{-1} + 0.773 \cdot 104\ g.mol^{-1}} \right) \cdot 0.773 = 7$$

**P2b:**

$$n(Tet) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Tet) \cdot M(Tet) + X(Styrene) \cdot M(Styrene)} \cdot X(Tet)$$

$$= \left( \frac{2650\ g.mol^{-1} - 261\ g.mol^{-1}}{0.217 \cdot 412\ g.mol^{-1} + 0.783 \cdot 104\ g.mol^{-1}} \right) \cdot 0.217 = 3$$

$$n(Styrene) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Tet) \cdot M(Tet) + X(Styrene) \cdot M(Styrene)} \cdot X(Styrene)$$

$$= \left( \frac{2600\ g.mol^{-1} - 261\ g.mol^{-1}}{0.217 \cdot 412\ g.mol^{-1} + 0.783 \cdot 104\ g.mol^{-1}} \right) \cdot 0.783 = 11$$

**P3:**

$$n(Acr) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Acr) \cdot M(Acr) + X(Styrene) \cdot M(Styrene)} \cdot X(Acr)$$

$$= \left( \frac{2500\ g.mol^{-1} - 261\ g.mol^{-1}}{0.279 \cdot 188\ g.mol^{-1} + 0.721 \cdot 104\ g.mol^{-1}} \right) \cdot 0.279 = 5$$

$$n(Styrene) = \frac{M_n(Polymer) - M(NMPgroup)}{X(Acr) \cdot M(Acr) + X(Styrene) \cdot M(Styrene)} \cdot X(Styrene)$$

$$= \left( \frac{2500\ g.mol^{-1} - 261\ g.mol^{-1}}{0.279 \cdot 188\ g.mol^{-1} + 0.721 \cdot 104\ g.mol^{-1}} \right) \cdot 0.721 = 13$$

## 5. SEM Images of Particle Synthesis Reactions

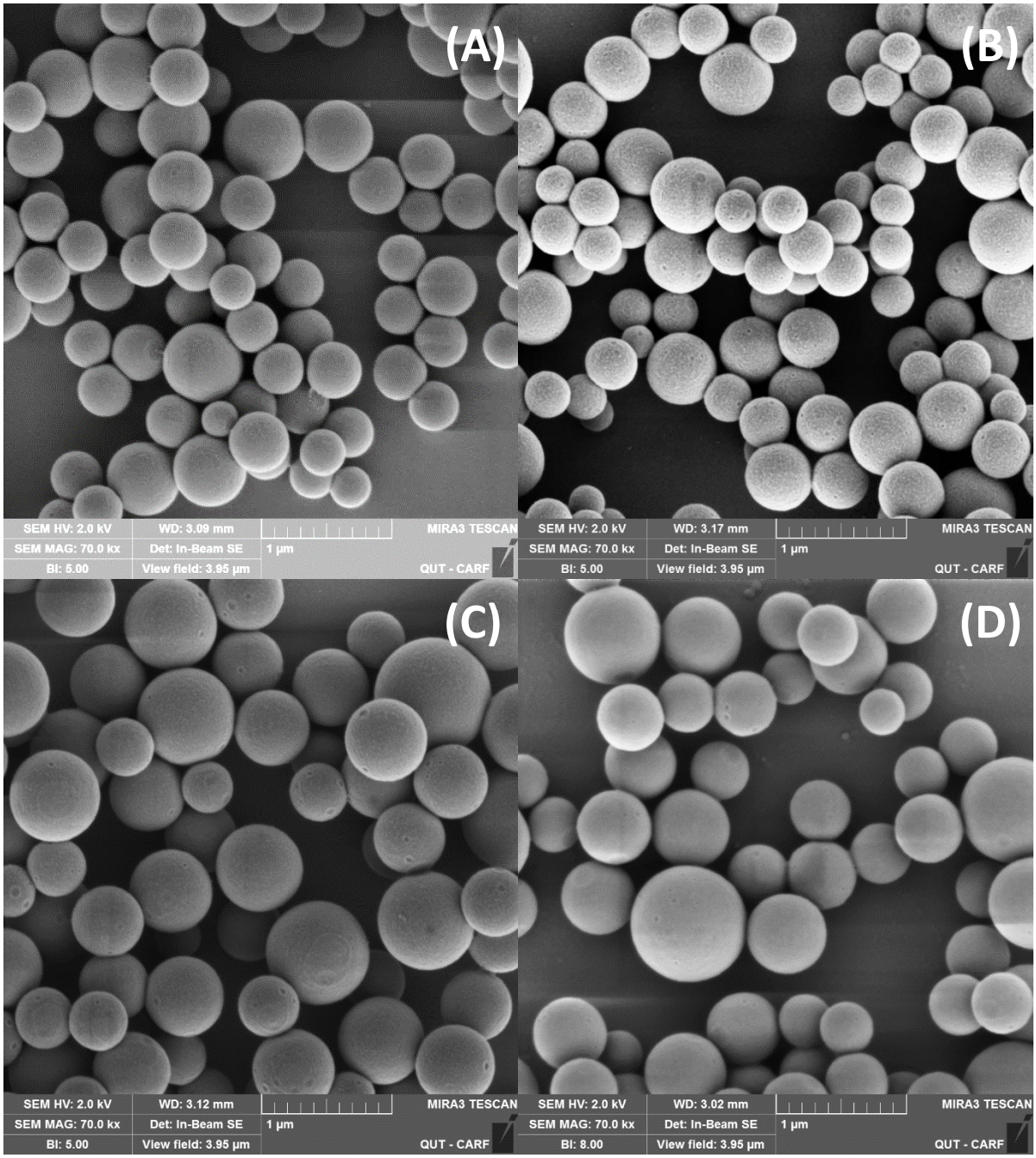



**Fig. S13**: SEM images of particle synthesis reactions with various ratios of **P2a** (Tet) and **P3** (Acr); (A) 1 mg $mL^{-1}$; 1:1 (B) 1 mg $mL^{-1}$; 1:2 (C) 2 mg $mL^{-1}$; 1:1 (D) 2 mg $mL^{-1}$; 1:2.

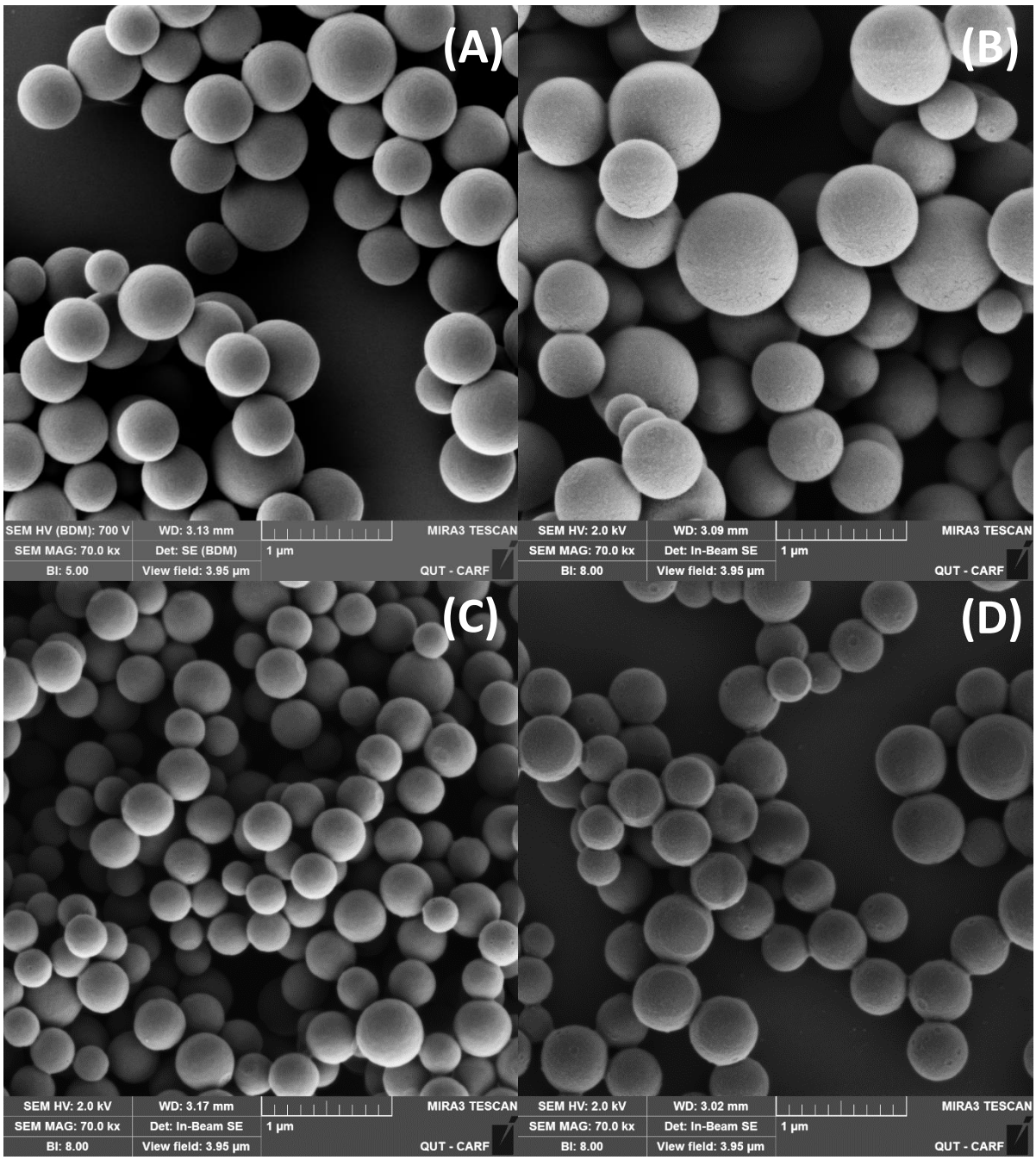



**Fig. S14**: SEM images of particle synthesis reactions with various ratios of THF and concentrations of **P2a** and **P3**; (A) 1.5 mg $mL^{-1}$; 10%THF (B) 3 mg $mL^{-1}$; 10% THF (C) 1.5 mg $mL^{-1}$; 20% THF (D) 3 mg $mL^{-1}$; 20% THF.

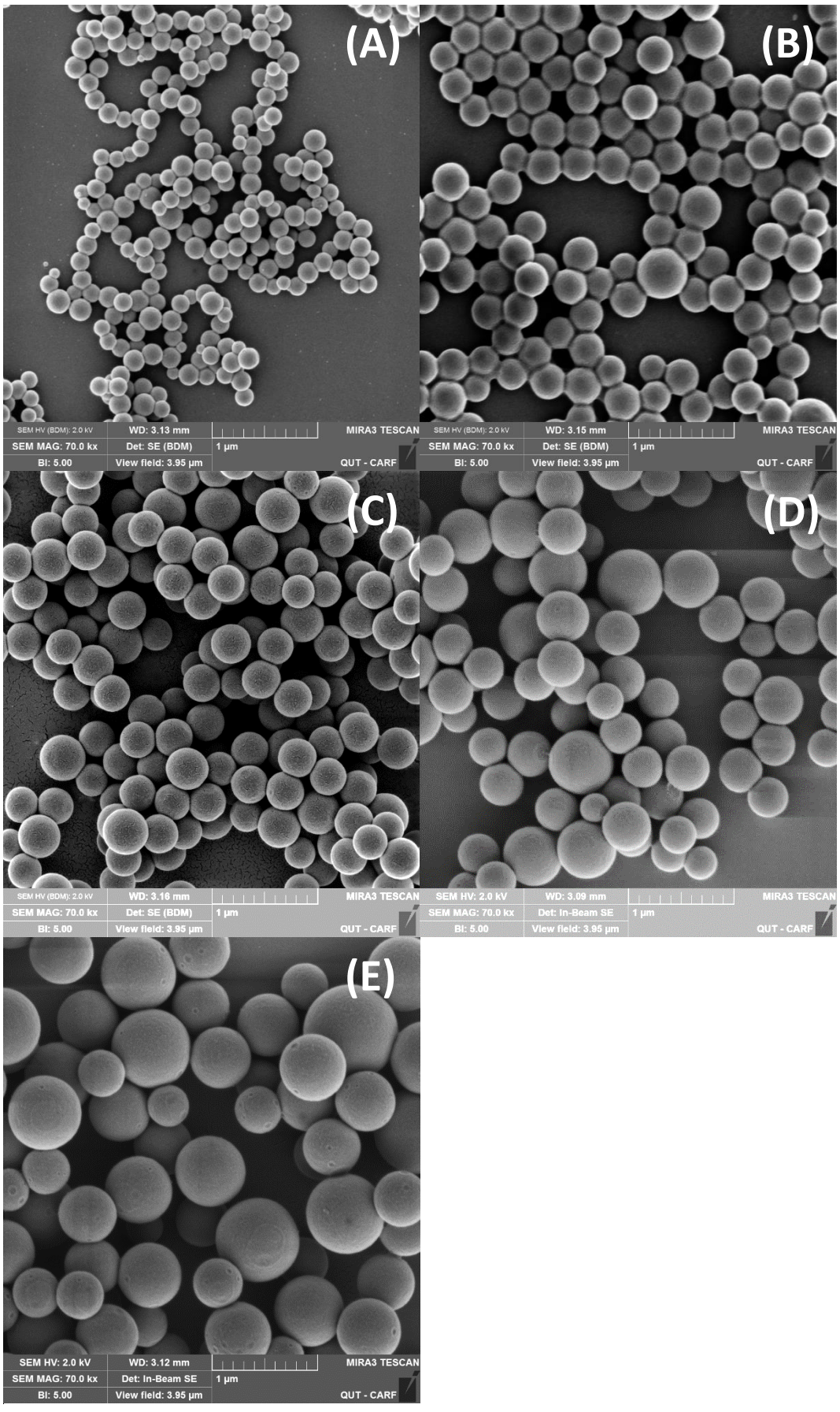



**Fig. S15**: SEM images of particle synthesis reactions at various total concentrations of **P2a** and **P3** at 1:1 mass ratio; (A) 0.25 mg $mL^{-1}$ (B) 0.5 mg $mL^{-1}$ (C) 0.67 mg $mL^{-1}$ (D) 1 mg $mL^{-1}$ (E) 2 mg $mL^{-1}$.

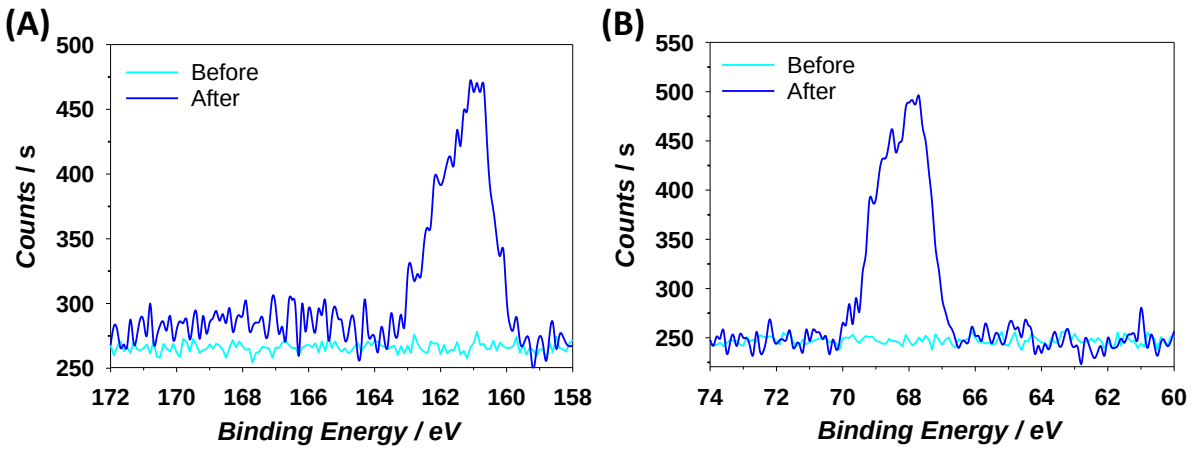



**Fig. S16**: XPS High resolution scans of microspheres (1:1 ratio) before and after encapsulation of 4-bromothiophenol: sulphur S *2p* (A); bromine Br *3d* (B).

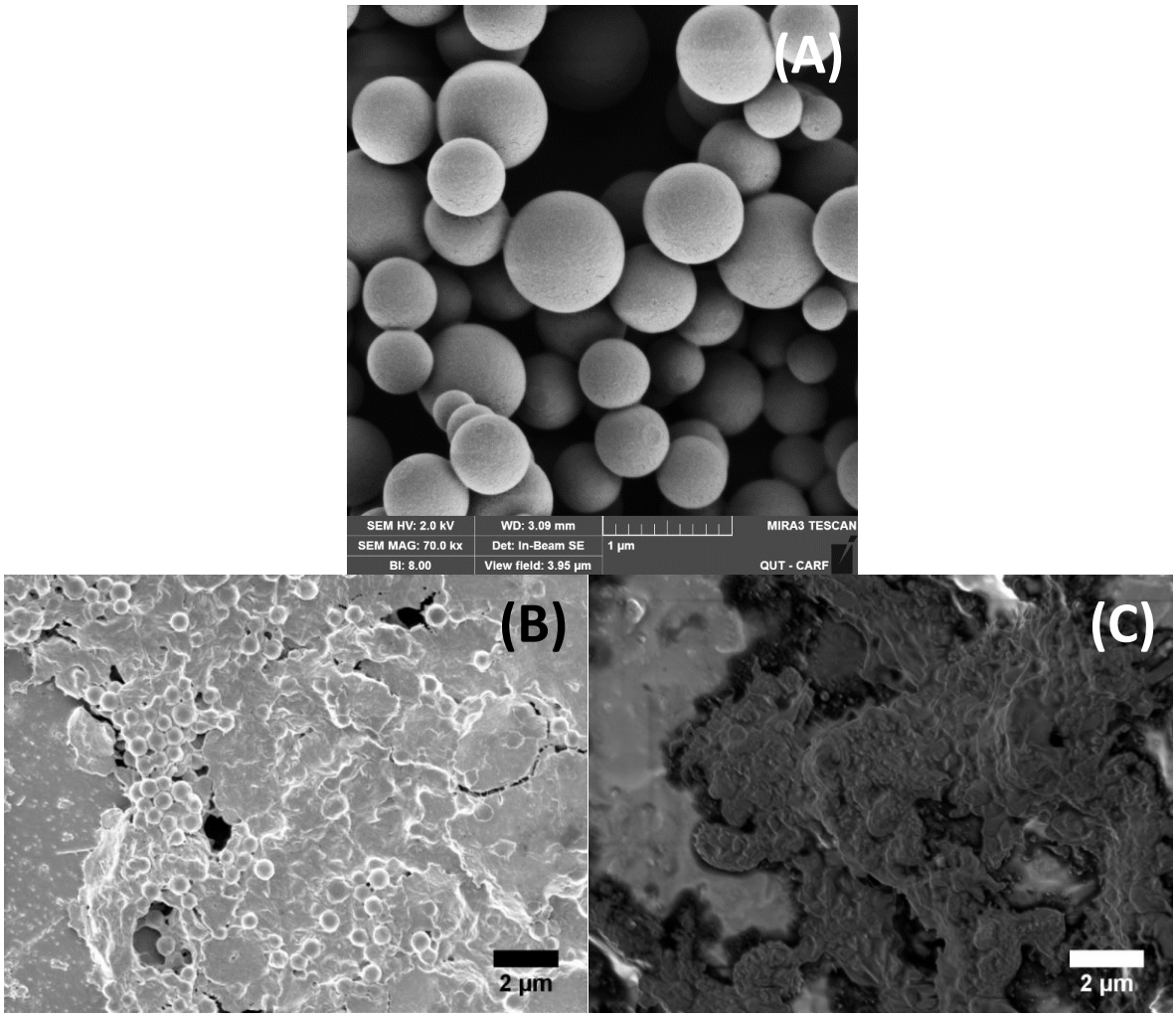



**Fig. S17**: SEM analysis of degradation of 3 mg $mL^{-1}$ 10% THF microspheres after addition of 0.1 M sodium hydroxide; (A) Before addition; (B) after 10 min; (C) after 3 h.

## 6 References


1. S. Harrisson, P. Couvreur and J. Nicolas, *Polym. Chem.,* 2011, **2**, 1859-1865.
2. C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns, A. S. Goldmann, M. Bastmeyer and C. Barner-Kowollik, *Adv. Mater.,* 2013, **25**, 6123-6127.