Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Self-Catalyzed Synthesis of Nano-Capsule and Its Application to Heterogeneous RCMP Catalyst and Nano-Reactor

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1. Experimental Section

Materials. Methyl methacrylate (MMA) (>99.8%, Tokyo Chemical Industry (TCI), Japan), 2-(dimethylamino)ethyl methacrylate (DMAEMA) (≥98.5%, TCI), 1-iodohexane (≥98%, Sigma-Aldrich, USA), poly(ethylene glycol) methyl ether methacrylate (PEGMA) (average molecular weight = 300) (98%, Sigma-Aldrich), benzyl methacrylate (BzMA) (>98%, TCI), ethylene glycol dimethacrylate (EGDMA) (≥98%, Sigma-Aldrich), acrylonitrile (AN) (>99%, TCI), styrene (St) (>99.8%, TCI), 2-iodo-2-methylpropionitrile (CP−I) (>95%, TCI), 2,2'-azobis(2,4-dimethylvaleronitrile) (V65) (95%, Wako Pure Chemical, Japan), 2,2′-azobis(2-methylpropionitrile) (AIBN) (95%, Wako), ethylene carbonate (>99%, TCI), acetone (≥99.5%, Fisher Scientific, USA), ethanol (≥99.5%, absolute, Fisher Scientific), tetrahydrofuran (THF) (>99.5%, Kanto Chemical, Japan), *N*,*N*-dimethylformamide (DMF) (>99.5%, Kanto), toluene (ACS reagent grade, VWR International), hexane (>99%, International Scientific, Singapore), trimethylsilyl methacrylate (TMSMA) (≥98.0%, TCI), 2-(methacryloyloxy)ethyl 2-(trimethylammonio)ethyl phosphate (MPC) (≥96.0%, TCI), 2-(methylthio)ethyl methacrylate (MTEMA) (≥96%, Sigma-Aldrich), 2,2,3,3,3-pentafluoropropyl methacrylate (PFPMA) (≥98.0%, TCI), 3-bromostyrene (Br-St) (≥97.0%, TCI), 4-chlorostyrene (Cl-St) (≥98.0%, TCI), glyceryl monomethacrylate (GMMA) (100%, Nippon Shokubai, Japan), phenylboronic acid (PBA) (≥97%, Sigma-Aldrich), anhydrous dichloromethane (DCM) (≥99.0%, TCI), and 4Å molecular sieves (Sigma-Aldrich) were used as received.

Measurement. The GPC analysis using THF as an eluent was performed on a Shimadzu i-Series Plus liquid chromatograph LC-2030c Plus (Kyoto, Japan) equipped with a Shodex (Japan) KF-804L mixed gel column (300 × 8.0 mm; bead size = 7 μm; pore size = 1500 Å) and a Shodex LF-804 mixed gel column (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å). The flow rate was 0.7 mL/min (40 °C). The GPC analysis using DMF as an eluent was performed on a Shimadzu LC-2030c Plus equipped with two Shodex LF-804 mixed gel columns (300 × 8.0 mm; bead size = 6 μm; pore size = 3000 Å) and a Shodex KD-802 (300 × 8.0 mm; bead size = 6 μm; pore size = 150 Å). The flow rate was 0.34 mL/min

(40 °C). The DMF eluent contained LiBr (10 mM). For both THF-GPC and for DMF-GPC, the sample detection was conducted using a refractive index detector (RID-20A) and the column system was calibrated with standard poly(methyl methacrylate)s (PMMAs).

The NMR spectra were recorded on Bruker (Germany) BBFO400 spectrometer (400 MHz) at ambient temperature. $CDCl_3$ and CD_3CN (Cambridge Isotope Laboratories, USA) were used as the solvents for the NMR analysis, and the chemical shift was calibrated using residual undeuterated solvents or tetramethylsilane (TMS) as the internal standard. The monomer conversions and the monomer compositions in the obtained polymers were determined with ^{1}H NMR.

Transmission electron microscopy (TEM) images were obtained on a JEM-1400 transmission electron microscope (JEOL, Japan) operated at 100 kV. The TEM grid was carbon-coated on 200 mesh (copper) (Ted Pella, USA).

The dynamic light scattering (DLS) measurement was carried out on a Malvern Zetasizer Nano ZSP (Worcestershire, UK). The test angle for the DLS analysis was 173° (backscattering detection). A mixture of water and ethanol and a mixture of THF and ethanol were used as the solvents.

Scanning electron microscopy (SEM) images were obtained on a JSM-7600F schottky field emission scanning electron microscope (JOEL, Japan) operated at 4.8 kV or 5 kV.

Confocal fluorescence microscopy images were taken with Zeiss LSM710 (Germany) using the filter set 38 under autoexposure.

Synthesis of Macroinitiator (PMMA-*r*-PC$_6$MAI-I). A mixture of MMA (7.6 g, 76.1 mmol), C$_6$MAI (1.46 g, 3.95 mmol), and CP−I (0.77 g, 3.95 mmol) was heated in a 50 mL flask at 60 °C under argon atmosphere with magnetic stirring. After 1 h, the mixture was cooled to room temperature and diluted with acetone (10 mL). The solution was dropped into a hexane/ethanol mixture (7/3 (v/v), 100 mL) for purification. The reprecipitation was repeated twice for complete removal of the monomers. The polymer was collected and dried in vacuo to give a (PMMA-*r*-PC$_6$MAI)−I as a yellow solid (yield =

36% (3.54 g) and M_n = 1700 and $Đ$ = 1.08 after purification). The molar ratio of the MMA and C_6MAI units in the polymer was calculated from the ^{1}H NMR spectrum (Figure S1 in ESI). The peak area ratio of $(b + c)/(a + d + e)$ was 4/18.93. The molar MMA/C_6MAI unit ratio in the copolymer is defined as x/y. From the relation of $(4y)/(3x+8y) = 4/18.93$, the ratio of x/y is calculated to be 79/21.

Self-catalyzed PISA. In a typical run, a mixture of BzMA monomer (1 g), a macroinitiator (PMMA-*r*-PC_6MAI)−I, V65, and ethanol was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, diluted with ethanol, water, or THF and then analyzed with DLS and TEM.

Polymerization using Catalytic Nano-Capsule. In a typical run, a mixture of a monomer (1 g), catalytic nano-capsule, CP−I, and solvent was heated in a Schlenk flask at 60–80 °C under argon atmosphere with magnetic stirring. After a prescribed time *t*, an aliquot (0.1 mL) of the solution was taken out by a syringe, cooled to room temperature, and analyzed with GPC and ^{1}H NMR.

Recycling of Catalytic Nano-Capsule. A mixture of MMA (4.5 g, 56 wt% of total reaction mixture, 100 equiv.), catalytic nano-capsule (0.5 g, 6 wt% of total reaction mixture, 0.2 equiv.), CP−I (1 equiv.), I_2 (0.0125 equiv.), AIBN (0.25 equiv.), and toluene (38 wt% of total reaction mixture) was heated in a Schlenk flask at 70 °C under argon atmosphere with magnetic stirring. After 9 h, the reaction mixture was cooled to room temperature. A part of the mixture was analyzed with GPC and ^{1}H NMR. The rest of the mixture was diluted with toluene and centrifuged to collect the catalytic nano-capsule. The catalytic nano-capsule was dried in vacuum overnight and subsequently used for the next MMA polymerization cycle.

Table S1. RCMPs of MMA using recycled catalytic nano-capsule.

Cycle[a]	$[MMA]_0/[CP–I]_0/[AIBN]_0/[I_2]$ (equiv.)[b]	Catalytic nano-capsule	T (ºC)	t (h)	Conv. (%)[c]	M_n ($M_{n,theo}$[d])	$Đ$
1	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	91	9800 (9100)	1.23
2	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	87	9200 (8700)	1.22
3	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	84	9400 (8400)	1.24
4	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	85	9500 (8500)	1.31
5	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	90	9500 (9000)	1.33
6	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	86	9800 (8600)	1.33
7	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	85	9800 (8500)	1.36
8	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	83	9600 (8300)	1.32
9	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	86	10400 (8600)	1.38
10	100/1/0.25/0.0125	6 wt% (0.2 equiv. C_6MAI unit)	70	9	86	10400 (8600)	1.39

[a] Polymerization cycle. [b] 56 wt% MMA, 6 wt% catalytic nano-capsule, and 38 wt% solvent (toluene). [c] Monomer conversions determined with ^{1}H NMR. [d] Theoretical M_n calculated according to ($[MMA]_0/[CP–I]_0$)×(monomer conversion).

Synthesis of PMMA in Catalytic Nano-Capsule. A mixture of catalytic nano-capsule (6 wt% of total reaction mixture) and toluene (38 wt% of total reaction mixture) was stirred at room temperature. After 2 h, a mixture of MMA (100 equiv., 56 wt% of total reaction mixture), CP–I (1 equiv.), AIBN (0.25 equiv.), and I_2 (0.025 equiv.) was added, and the whole mixture was stirred for another 2 h at room temperature. The whole mixture was then heated at 70 ºC for 6 h. The mixture was cooled to room temperature, stirred with excess toluene, and centrifuged to collect the nano-capsule. The collected nano-capsule was dried in vacuum. For the repeated washing study, the collected (PMMA-entrapped) nano-capsule was washed thrice in excess acetone and subsequently thrice in excess THF. Each wash step was performed with magnetic stirring in the solvent to ensure the nano-capsule to remain in suspension and with centrifugation to collect the nano-capsule. The nano-capsule collected after the final THF wash was dried in vacuum.

Synthesis of PPEGMA–I Macroinitiator in Catalytic Nano-Capsule. A mixture of catalytic nano-capsule (6 wt% of total reaction mixture) and toluene (36 wt% of total reaction mixture) was stirred at room temperature. After 2 h, a mixture of PEGMA (100 equiv., 58 wt% of total reaction mixture), CP–I (2 equiv.), and V65 (1 equiv.) was added, and the whole mixture was stirred for another 2 h at room temperature. The whole mixture was then heated at 60 °C for 0.5 h. The mixture was cooled to room temperature, stirred with excess toluene, and centrifuged to collect the nano-capsule. The collected nano-capsule was dried in vacuum.

Synthesis of Amphiphilic Block Copolymer in Catalytic Nano-Capsule. A mixture of PPEGMA–I containing catalytic nano-capsule (12 wt% of total reaction mixture, 1 equiv. of PPEGMA–I (M_n = 6500)), NMA (38 wt% of total reaction mixture, 100 equiv.), and toluene (50 wt% of total reaction mixture) was stirred at room temperature. After 2 h, the mixture was heated at 70 °C for 24 h. The mixture was cooled to room temperature, stirred with excess toluene, and centrifuged to collect the nano-capsule. The collected nano-capsule was dried in vacuum.

Synthesis of (2-Phenyl-1,3,2-dioxaborolan-4-yl)methyl Methacrylate (PDBMA). We synthesized (2-phenyl-1,3,2-dioxaborolan-4-yl)methyl methacrylate (PDBMA) according to the literature.[1] A mixture of phenylboronic acid (21.75 mmol), GMMA (21.75 mmol), and dry dichloromethane (200 mL) in the presence of 20 g 4Å molecular sieves was stirred at room temperature over 24 h. The mixture was purified through filtering, centrifugation, and filtering again and then concentrated to give PDBMA as a pale-yellow liquid in a nearly quantitative yield. The product was characterized by ^{1}H and ^{11}B

NMR. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.81 (d, J = 6.8 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.4 Hz, 7.4Hz, 2H), 6.09 (s, 1H), 5.54 (s, 1H), 4.85-4.79 (m, 1H), 4.44 (dd, J = 8.8 Hz, 8.8 Hz, 1H), 4.35 (dd, J = 11.9, 3.9 Hz, 1H), 4.28 (dd, J = 11.9, 4.4 Hz, 1H), 4.18 (dd, J = 9.2, 6.1 Hz, 1H), 1.90 (s, 3H); ^{11}B-NMR (400 MHz, $CDCl_3$, δ): 29.3.

Synthesis of Multi-Elemental Polymer in Catalytic Nano-Capsule. A mixture of PPEGMA–I containing catalytic nano-capsule (10.3 wt% of total reaction mixture, 1 equiv. of PPEGMA–I (M_n = 6500)), PDBMA (7.8 wt%, 20 equiv.), TMSMA (0.3 wt%, 20 equiv.), MPC (9.4 wt%, 20 equiv.), MTEMA (5.1 wt%, 20 equiv.), PFPMA (6.9 wt%, 20 equiv.), Br-St (5.8 wt%, 20 equiv.), Cl-St (4.4 wt%, 20 equiv.), and toluene (50 wt% of total reaction mixture) was stirred at room temperature. After 2 h, the mixture was heated at 70 ºC for 24 h. The mixture was cooled to room temperature, stirred with excess toluene, and centrifuged to collect the nano-capsule. The collected nano-capsule was dried in vacuum.

2. Additional Data

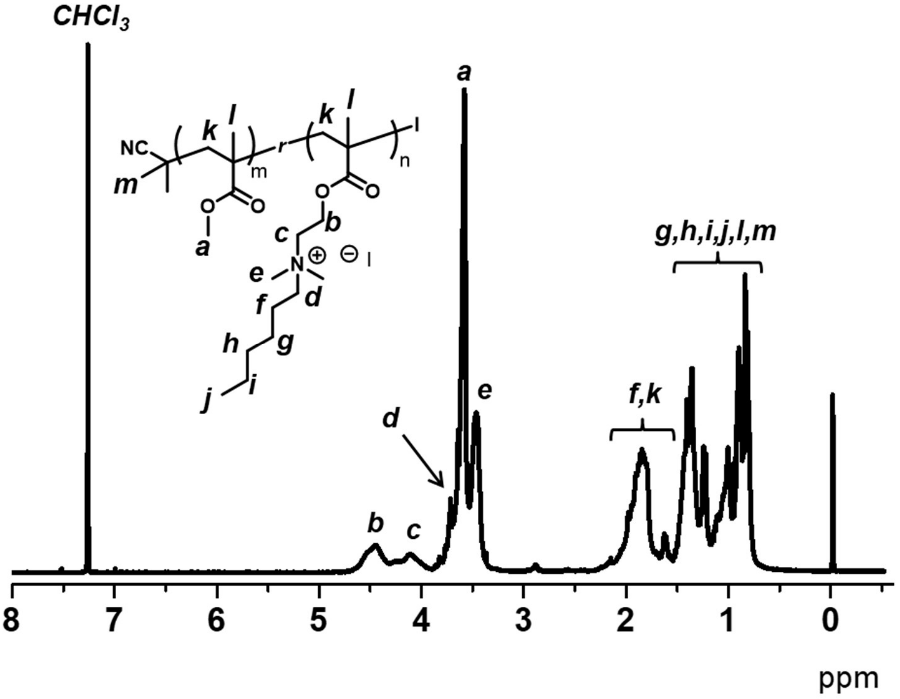


Figure S1. ^{1}H NMR spectrum of PMMA-*r*-PC$_6$MAI (Table 1) (400 MHz, 298 K, CDCl$_3$).

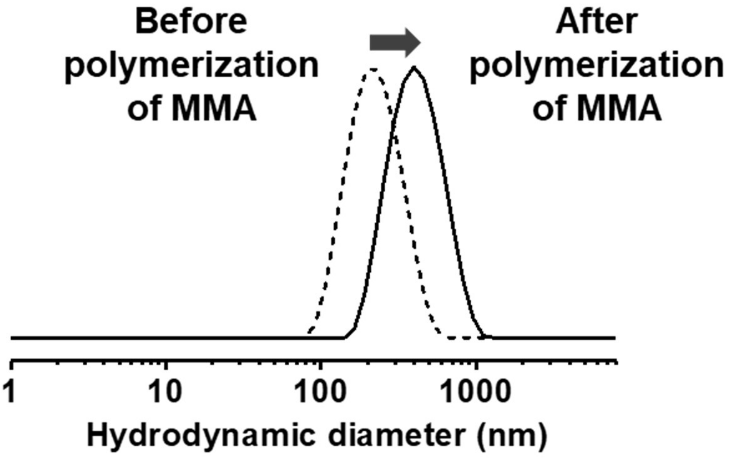


Figure S2. DLS curves of catalytic nano-capsule before (dashed line) and after (solid line) the polymerization of MMA inside the nano-capsule.

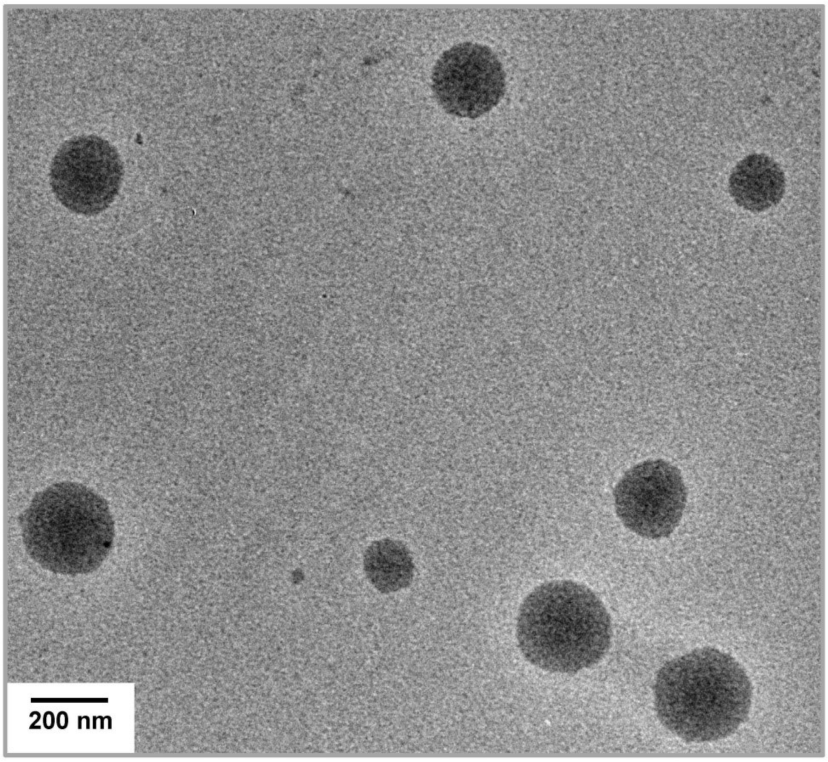


Figure S3. TEM image of PMMA–I containing catalytic nano-capsule after repeated washing.

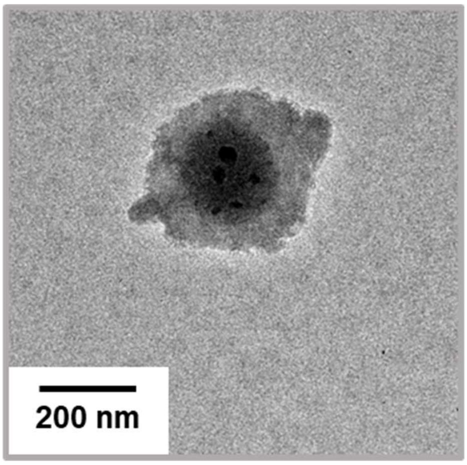


Figure S4. TEM images of PPEGMA–I containing catalytic nano-capsule.

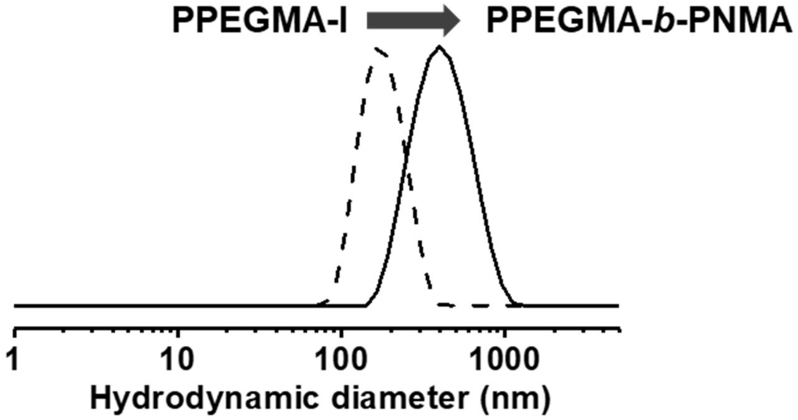


Figure S5. DLS curves of catalytic nano-capsule containing PPEGMA–I macroinitiator (dashed line) and PPEGMA-*b*-PNMA (solid line).

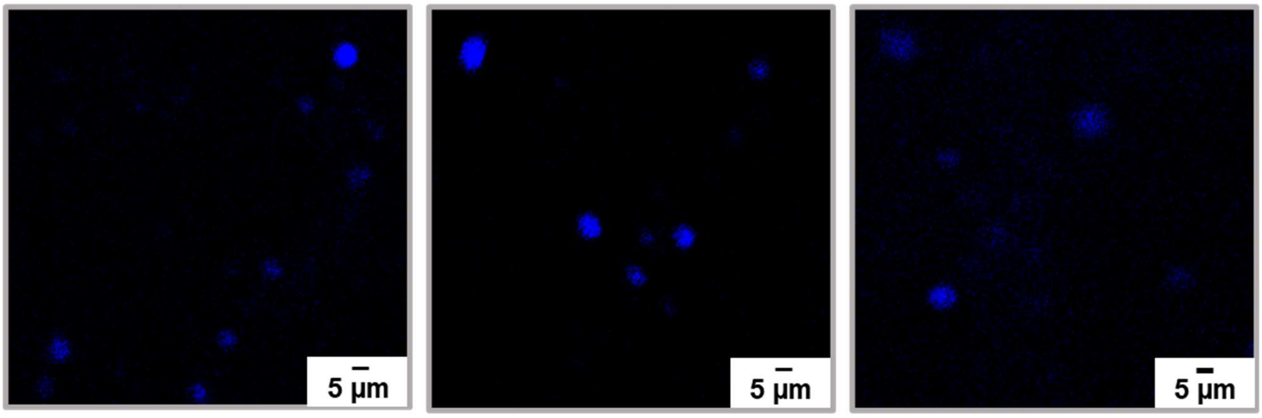


Figure S6. Confocal fluorescence images of PPEGMA-*b*-PNMA-loaded catalytic nano-capsule (examples additional to Figure 7b).

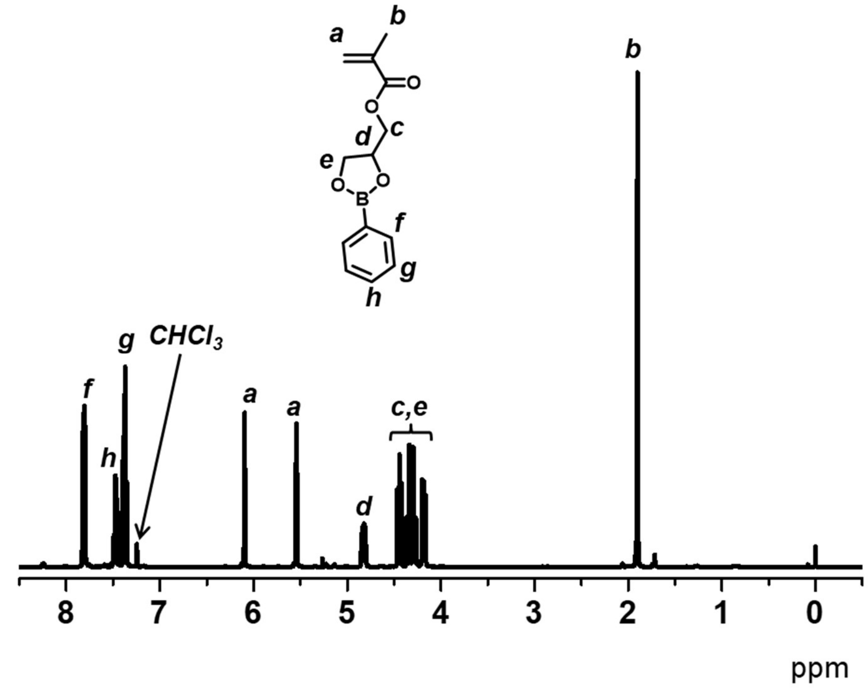


Figure S7. ^{1}H NMR spectrum of PDBMA monomer (400 MHz, 298 K, $CDCl_3$).

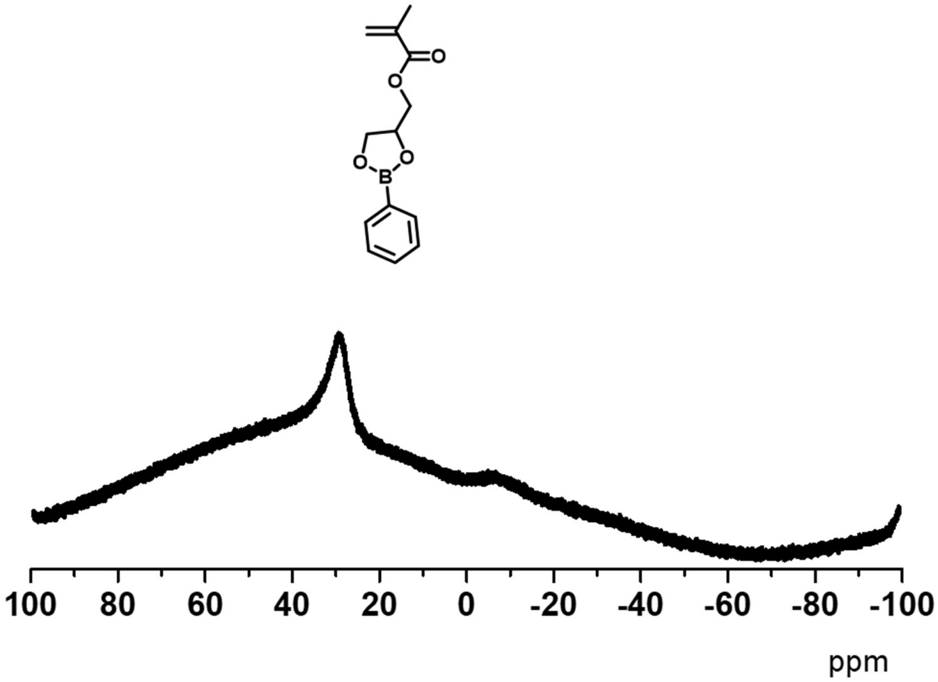


Figure S8. ^{11}B NMR spectrum of PDBMA monomer (400 MHz, 298 K, $CDCl_3$).

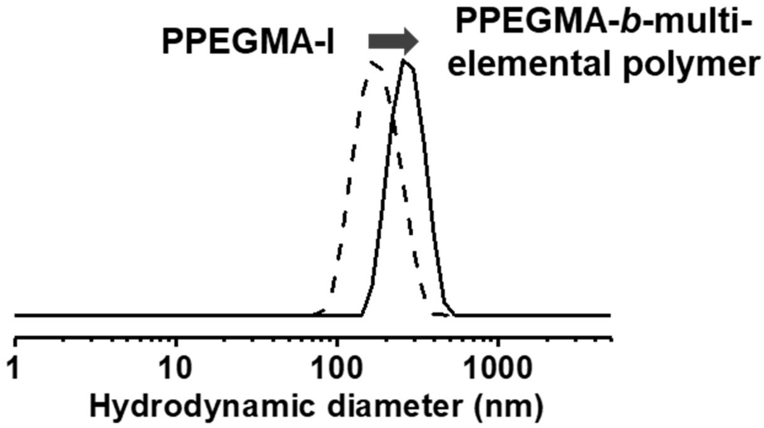


Figure S9. DLS curves of catalytic nano-capsule containing PPEGMA–I macroinitiator (dashed line) and PPEGMA-*b*-multi-elemental polymer (solid line).

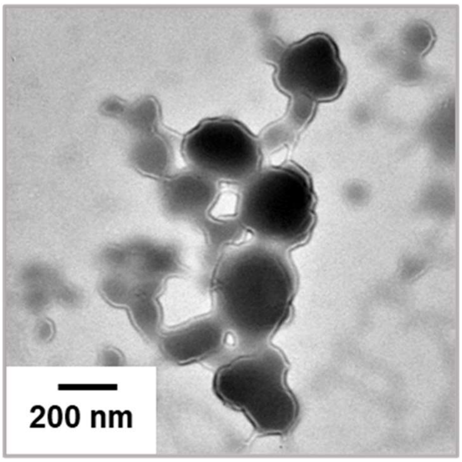
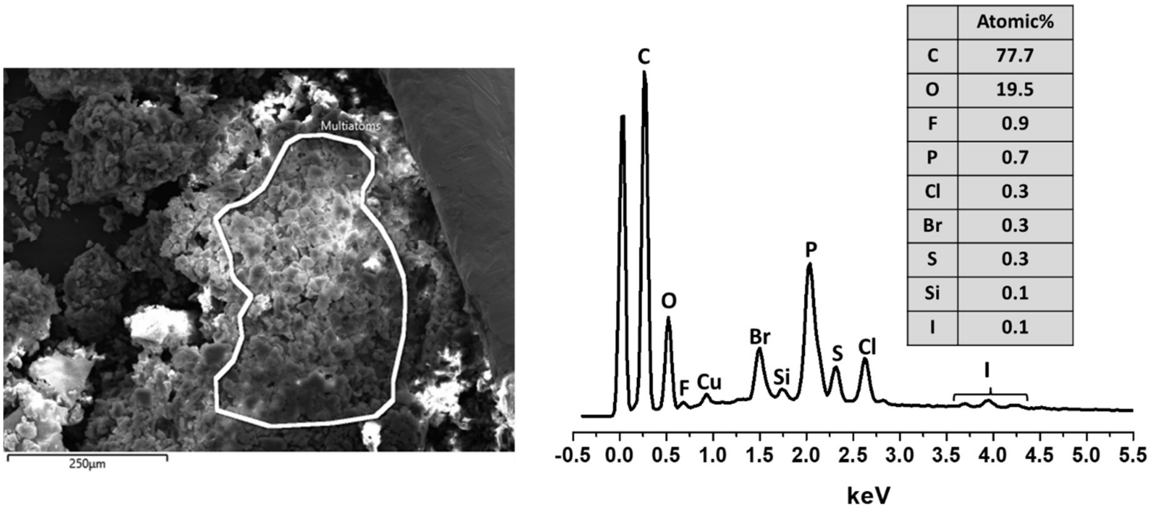


Figure S10. TEM image of PPEGMA-*b*-multi-element polymer nano-capsule.



	Atomic%
C	77.7
O	19.5
F	0.9
P	0.7
Cl	0.3
Br	0.3
S	0.3
Si	0.1
I	0.1

Figure S11. (a) Electron image of selected area for elemental scanning spectrum and (b) spectrum of multi-element polymer nano-capsule obtained from SEM-EDS.

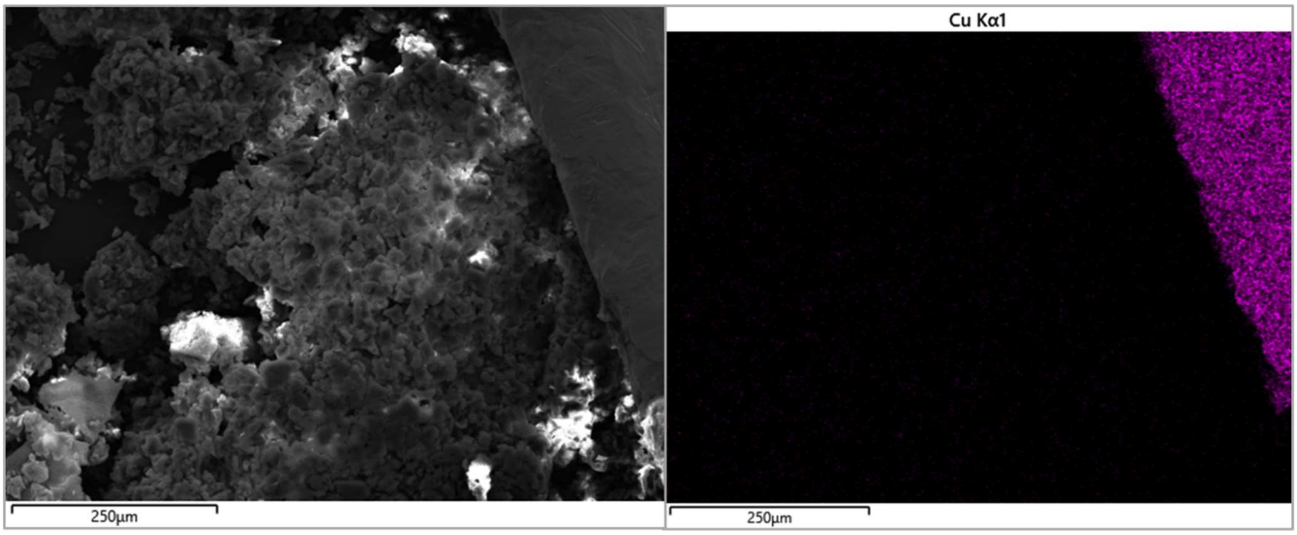


Figure S12. SEM-EDS elemental mapping of copper for PPEGMA-*b*-multi-elemental polymer nano-capsule.

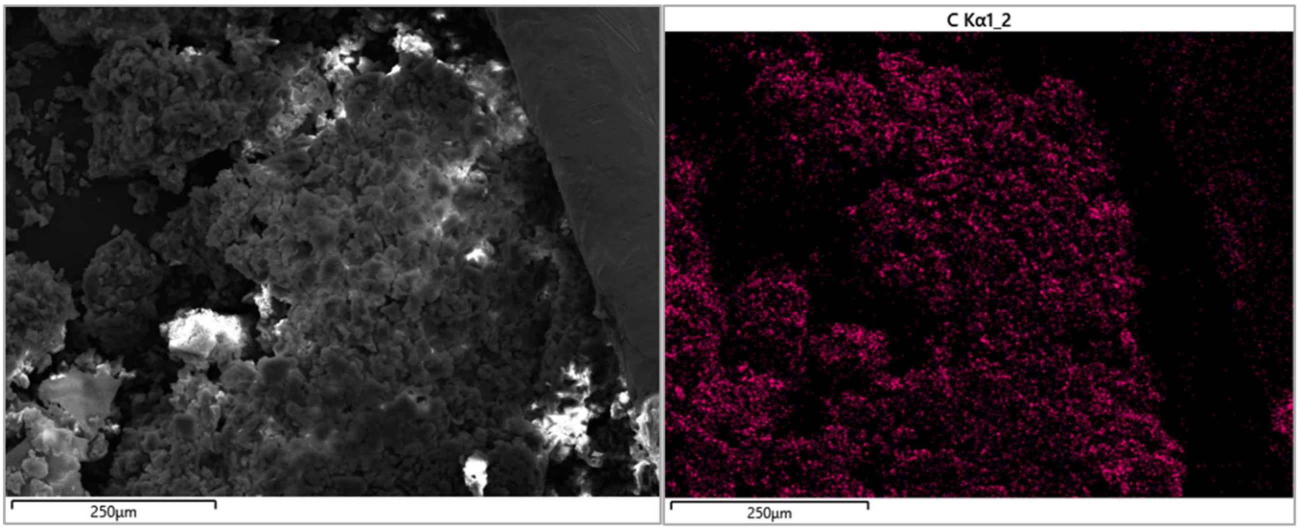


Figure S13. SEM-EDS elemental mapping of carbon for PPEGMA-*b*-multi-elemental polymer nano-capsule.

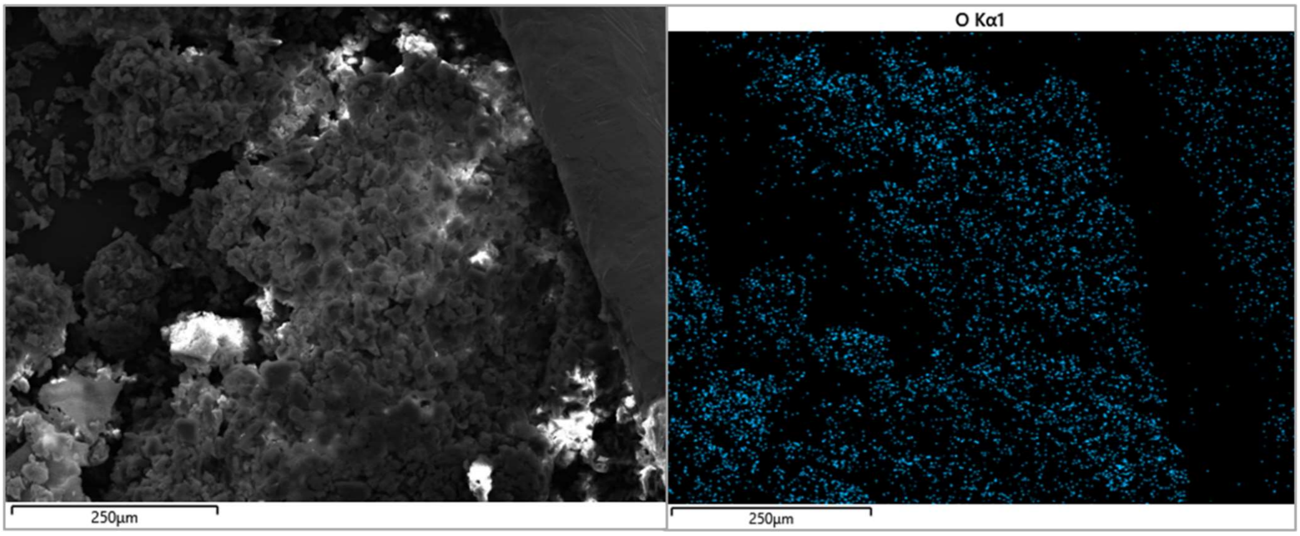


Figure S14. SEM-EDS elemental mapping of oxygen for PPEGMA-*b*-multi-elemental polymer nano-capsule.

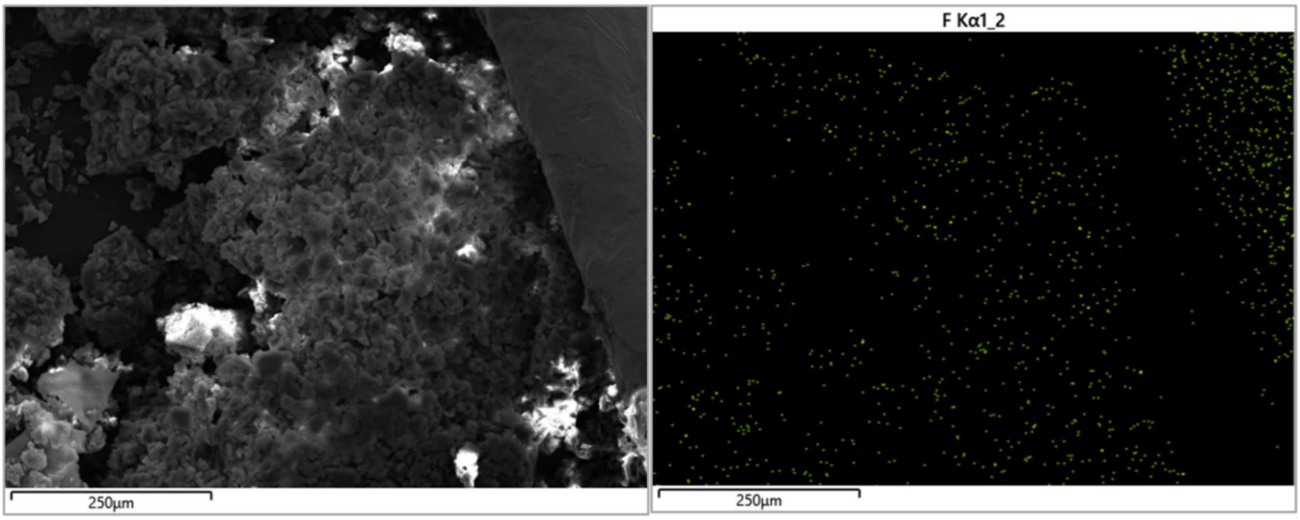


Figure S15. SEM-EDS elemental mapping of fluorine for PPEGMA-*b*-multi-elemental polymer nano-capsule.

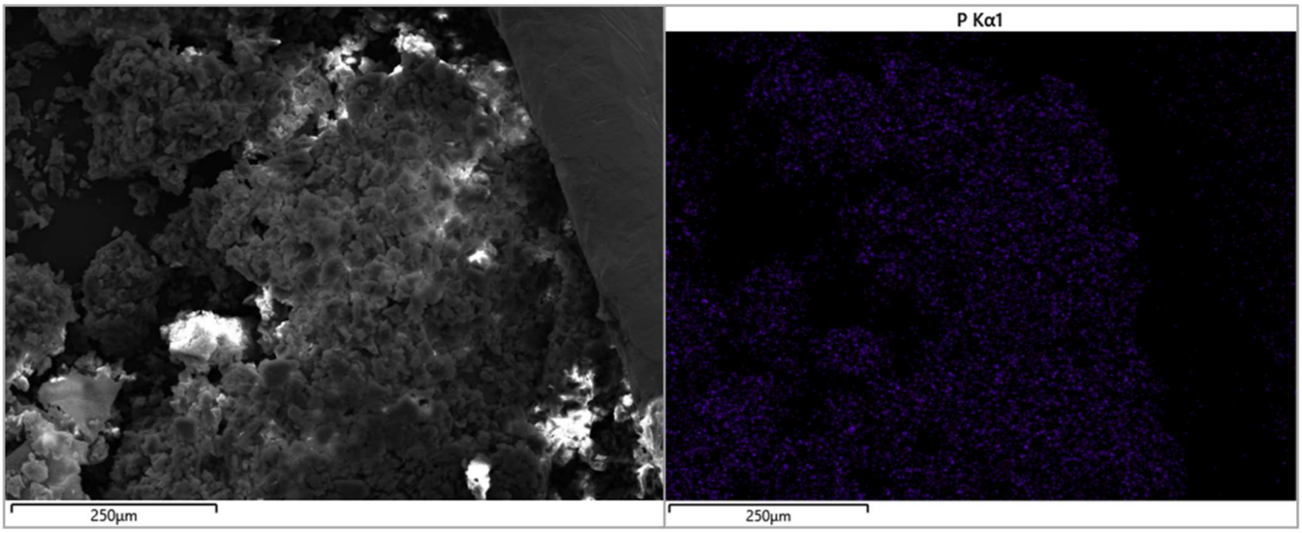


Figure S16. SEM-EDS elemental mapping of phosphorus for PPEGMA-*b*-multi-elemental polymer nano-capsule.

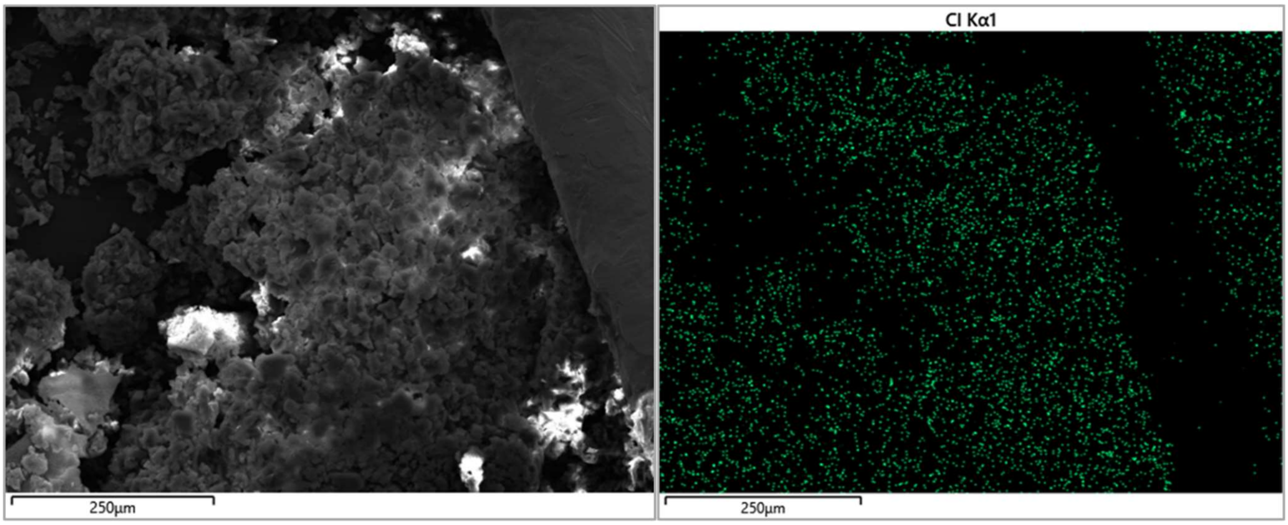


Figure S17. SEM-EDS elemental mapping of chlorine for PPEGMA-*b*-multi-elemental polymer nano-capsule.

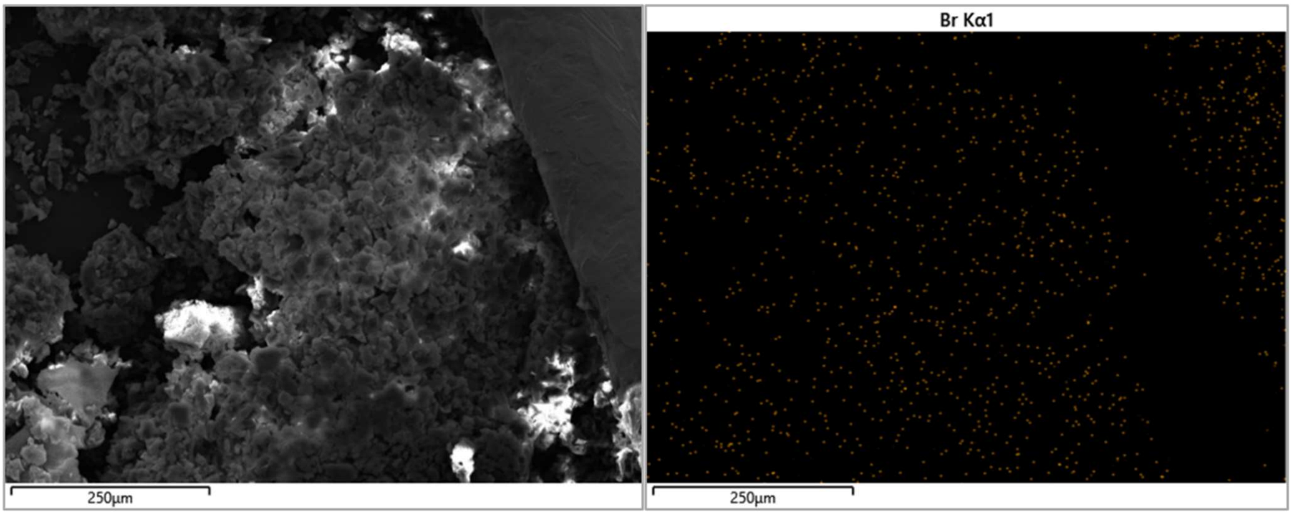


Figure S18. SEM-EDS elemental mapping of bromine for PPEGMA-*b*-multi-elemental polymer nano-capsule.

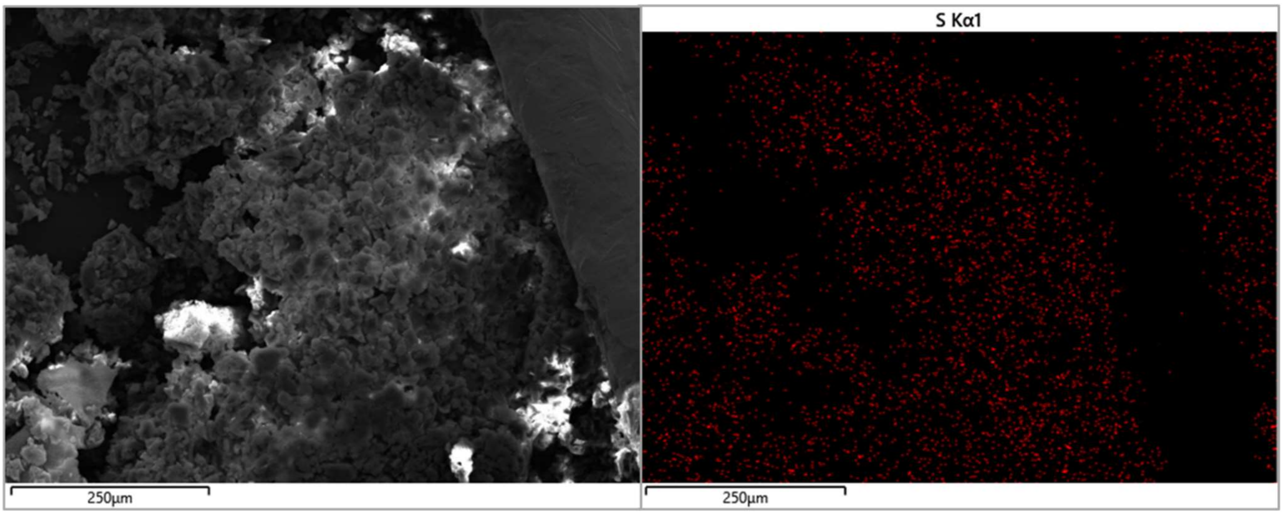


Figure S19. SEM-EDS elemental mapping of sulfur for PPEGMA-*b*-multi-elemental polymer nano-capsule.

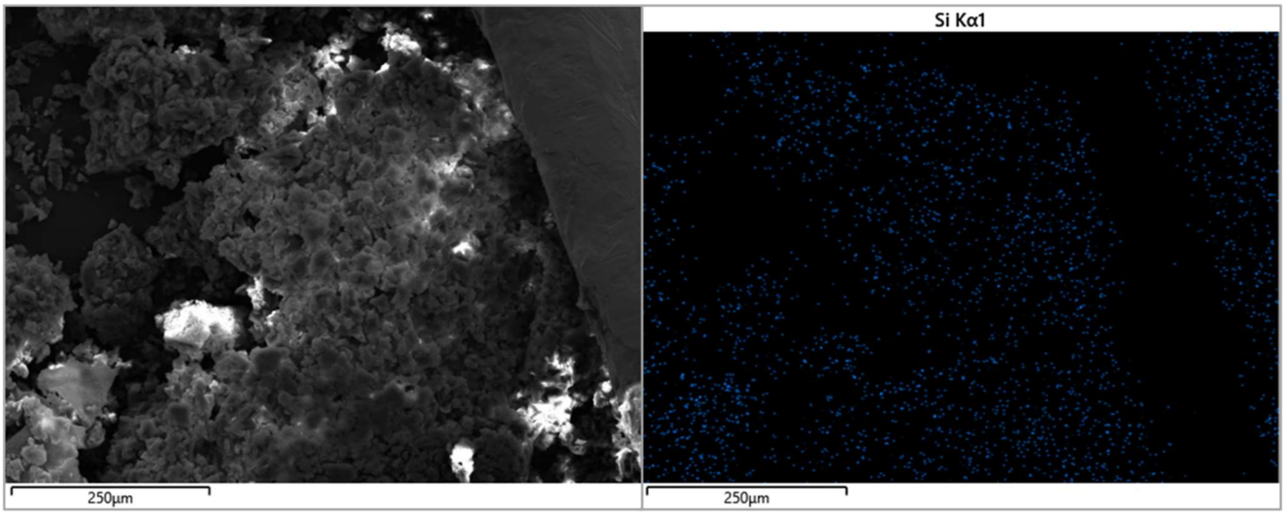


Figure S20. SEM-EDS elemental mapping of silicon for PPEGMA-*b*-multi-elemental polymer nano-capsule.

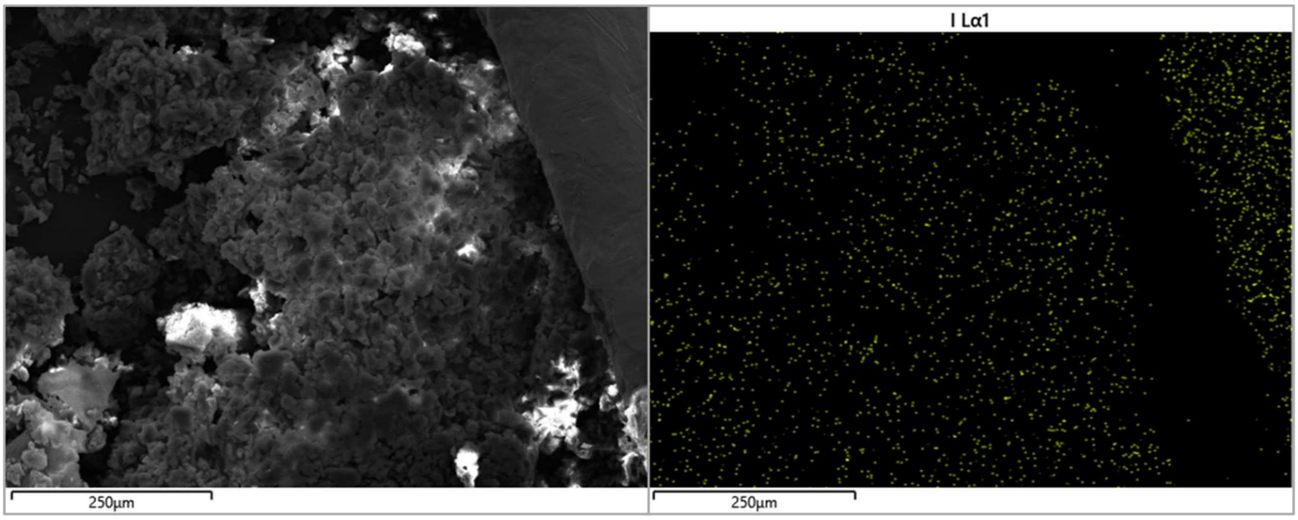
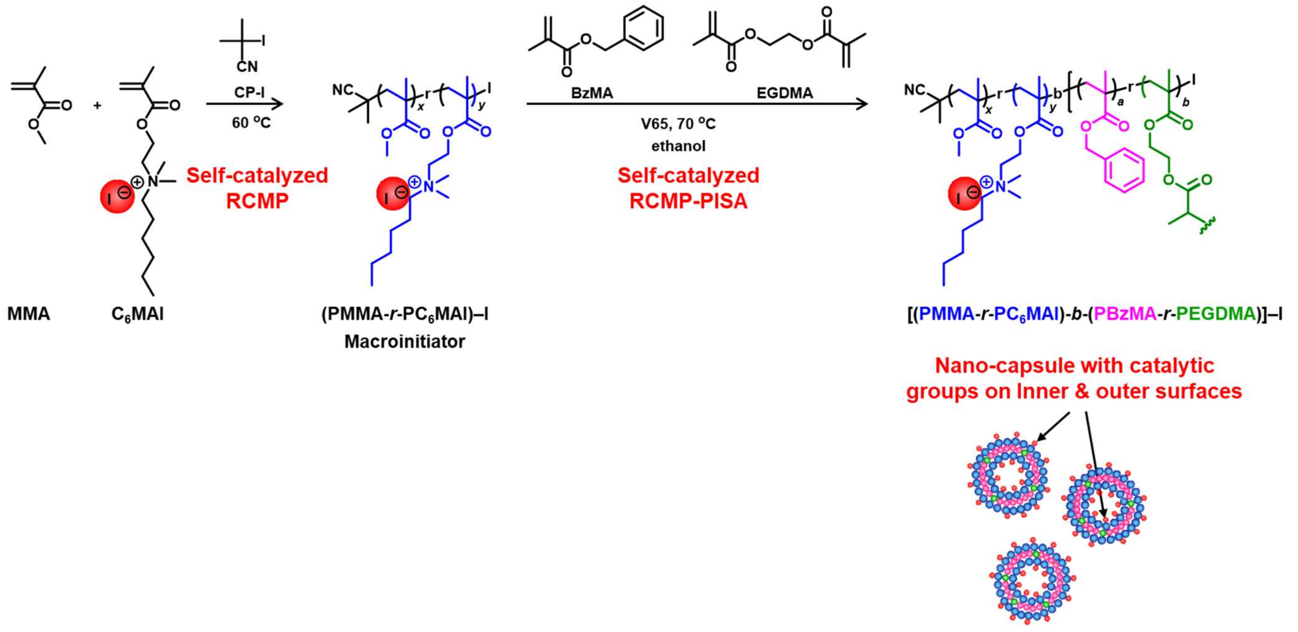


Figure S21. SEM-EDS elemental mapping of iodine for PPEGMA-*b*-multi-elemental polymer nano-capsule.



Scheme S1. Self-catalyzed synthesis of crosslinked nano-capsule via RCMP-PISA.

3. Reference

1. P. Yuan, C. Cai, J. Tang, Y. Qin, M. Jin, Y. Fu, Z. Li, X. Ma, *Adv. Funct. Mater.*, 2016, **26**, 5930–5939.