Supporting Information

Degradable Polymeric Nanomaterials with High Solid Content and Multiple Morphologies by Polymerization-induced Self-assembly

Jing Liu,[a,c] Wen-Jun Wu,[b,c] Xiao-Li Sun,*[b,c] Qing-Rong Qian[b,c] and Li-Ren Xiao*[a,c]

[a] College of Chemistry and Material Science, Fujian Normal University, Fuzhou 350007, China. E-mail: xlr1966@fjnu.edu.cn

[b] College of Environmental Science and Engineering, Fujian Normal University, Fuzhou 350007, China. E-mail: sunxiaoli@fjnu.edu.cn

[c] Engineering Research Center of Polymer Green Recycling of Ministry of Education, Fujian Key Laboratory of Pollution Control & Resource Reuse, Fujian Normal University, Fuzhou 350007, China.

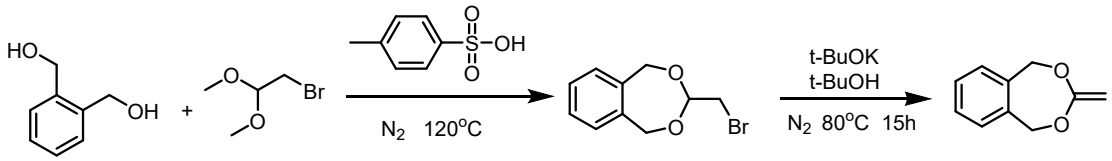
Contents:

1. Materials

Styrene (St, 99.5%) was passed through neutral alumina column before use. Azobisisobutyronitrile (AIBN, 98%) was recrystallized in methanol. *S*-1-dodecyl-*S*-(*α,α′*-dimethyl-*α′′*-acetic acid) trithiocarbonate (TTC) as the chain transfer agent was synthesized according to literature procedures.[1] All other reactants and solvents were used as received.

2. Experimental

2.1 Synthesis of 5,6-Benzo-2-methylene-1,3-dioxepane (BMDO)



Scheme S1. The synthesis scheme of BMDO.

Synthesis of 5,6-Benzo-2-(bromomethyl)-1,3-dioxepane (BBMDO). A mixture of 27.6 g (0.2 mol) of 1,2-benzenedimethanol, 33.8 g (0.2 mol) of bromoacetaldehyde dimethyl acetal, and 276.92 mg of p-toluene-sulfonic acid was heated at 120°C under nitrogen in a flask until the expected amount methanol was collected. Afterwards, the crude product was solidified on cooling the reaction mixture to room temperature. The product was dissolved in 100 ml $CHCl_3$ and washed with 100 ml saturated $NaHCO_3$ solution and then 100 ml water. The organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain a light brown solid. The solid was dissolved in 200 ml cyclohexane and recrystallize to obtain white crystals (BBMDO), resulting in 35.3045 g (72.64%). ^{1}H nuclear magnetic resonance (NMR) (400 MHz, $CDCl_3$, δ): 3.44 (d, -CH_2Br, 2H), 4.93 (s, C_6H_4(CH_2O)$_2$-, 4H), 5.12 (t, (-CH_2O)$_2$C$H$$CH_2$Br, 1H), 7.17-7.27 (m, Ar, 4H).

Synthesis of 5,6-Benzo-2-methylene-1,3-dioxepane (BMDO). A mixture of 15.4 g (0.14 mol) of t-BuOK and 35.30 g (0.15 mol) of BBMDO were allowed to react in the presence of 200 ml t-BuOH under nitrogen at 80°C for 15 h. After the reaction cooled to room temperature, 200 ml ether was added. The solid was removed by filtration, and the solvent was removed under reduced pressure. 17.10 g (72.77%) of white crystal product was obtained by distillation under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.76 (s, (-CH_2O)$_2$C=CH_2), 2H), 5.09 (s, C_6H_4(CH_2O)$_2$-, 4H), 7.10-7.14 (m, Ar, 2H), 7.27-7.29 (m, Ar, 2H).

2.2 Synthesis of Poly(4-vinyl pyridine) Macro-CTA (P4VP)

A typical solution copolymerization procedure by Reversible Addition−Fragmentation Chain Transfer (RAFT) Polymerization was conducted as follows for $P4VP_{75}$ macro-CTA. A mixture of 4-vinylpyridine (19.4643 g, 0.1 mol), CTA (0.708 g, 1mmol), AIBN (0.0310 g, 0.1mol) and isopropanol (6.0 mL) were added into a Schlenk tube. After three cycles of freeze-pump-thaw, the tube was sealed under high vacuum, immersed in an oil bath at 80°C and kept stirring for 6 hours. Afterwards, the Schlenk tube was taken out and immersed in an ice-water bath to terminate the reaction. The reaction solution was diluted with dichloromethane, and the precipitation was repeated 3 times with anhydrous petroleum ether as the precipitant. After filtration and vacuum drying, 10.68 g P4VP was obtained as a pale-yellow powder, and the yield was 54.8%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.85-0.94 (broad, −CH_3, 3H), 1.19-1.30 (broad, −COOH, 1H), 1.32-1.97 (broad, −CH_2CH−, 1H), 2.08-2.54 (broad, −CHCH_2, 2H), 3.21-3.32 (broad, −CH_2−$C_{12}H_{25}$, 2H), 6.18-6.75

(broad, Ar, 2H), 8.15-8.68 (broad, Ar, 2H).

2.3 Synthesis of Poly(4-vinyl pyridine)-*b*-poly[(styrene)-*co*-(5,6-benzo-2-methylene-1,3-dioxepane] (P4VP-*b*-P(St-*co*-BMDO)) nanomaterials by polymerization-induced self-assembly (PISA)

Macromolecular chain transfer agent P4VP, initiator AIBN, dispersant methanol, monomer styrene and BMDO were added to 10 mL Schlenk tube with magnets. After three cycles of freeze-pump-thaw procedure, it was placed in an oil bath at 80°C and kept stirring for 24 h. Then the Schlenk tube was put into an ice-water bath to cool down to terminate the reaction. To investigate the morphologies, 10 μL reaction solution was directly dispersed in 1 mL methanol and a drop of the solution was placed onto carbon coated copper grids for TEM or single side polished wafers for SEM. For the characterization of chemical structure, part of the reaction solution was precipitated in excess petroleum ether for three times, and the powder was dried in vacuum at room temperature to obtain pale yellow P4VP-*b*-P(St-*co*-BMDO).

2.4 Degradation of P4VP-*b*-P(St-*co*-BMDO)

In a 20 mL vial, 50 mg of purified copolymer was dissolved in 2 mL THF. After solubilization, 4 mL of potassium hydroxide solution (KOH, 5 wt %) in methanol was added. The mixture was stirred at room temperature. After a certain period of time, the mixture was dialyzed against methanol, and then the solvent was removed under reduced pressure. Degradation products were obtained after vacuum drying at room temperature. The molecular weight of the degradation product was analysed by gel permeation chromatography *(GPC)*, and the structure was analysed by ^{1}H NMR.

3. Characterizations

NMR spectroscopy was performed in 5 mm diameter tubes in $CDCl_3$ at 25°C on a Bruker 400 MHz spectrometer at 400 MHz. The chemical shift scale was calibrated based on the internal solvent signals (δ = 7.26 ppm).

GPC was performed at 50°C with two columns from Agilent 1260 infinity Ⅱ equipped with a G7110B isocratic pump and G7162A refractive index detector, using N,N-Dimethylformamide (DMF) as eluent at a flow rate of 1.0 mL·min^{-1}. A conventional calibration curve was based on polystyrene standards. This technique allowed M_n (number-average molecular weight), M_w (weight-average molecular weight), and M_w/M_n (polydispersity index PDI) to be determined. GPC of degraded copolymers was performed in DMF.

The Hitachi 8100 field emission scanning electron microscope (FESEM) and transmission Electron microscopy (TEM) were used for the morphology of the nanoparticles. FESEM was performed with Hitachi 8100 operating at 5 kV and 10 μA, respectively. Samples were prepared by placing a drop of polymer micelle solution on single side polished wafers. TEM was performed by using a JEOL-2100F and a JEM-f200 operating at 200 kV. Diluted block copolymer nanoparticle suspensions were prepared by placing a drop of polymer micelle solution onto carbon coated copper grids.

Differential Scanning Calorimeter (DSC) was used to measure the glass transition temperature (T_g) of the copolymer by a TA Instruments Q20 under nitrogen with a heating rate of 10°C /min.

4. Figures and Tables

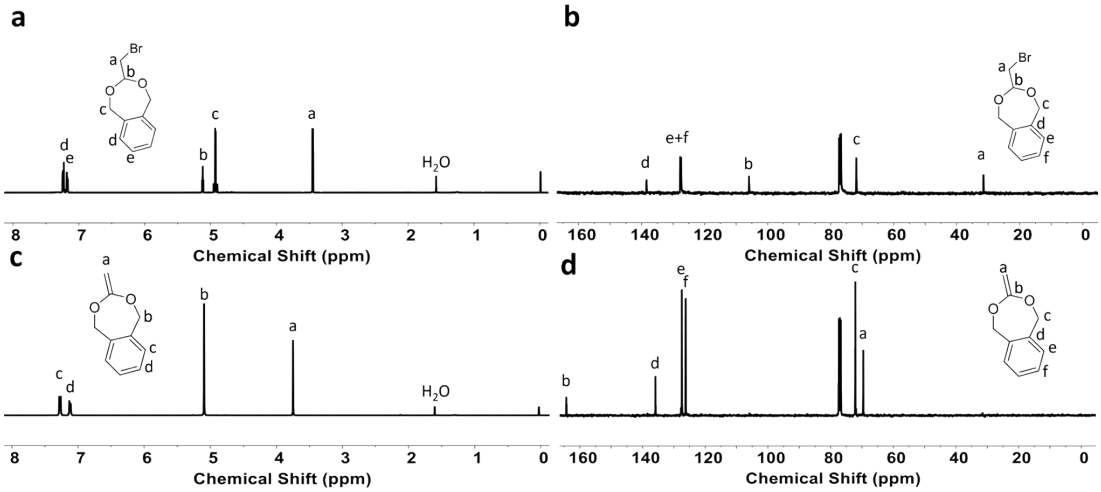


Figure S1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of BBMDO; ^{1}H NMR (c) and ^{13}C NMR (d) spectra of BMDO in $CDCl_3$.

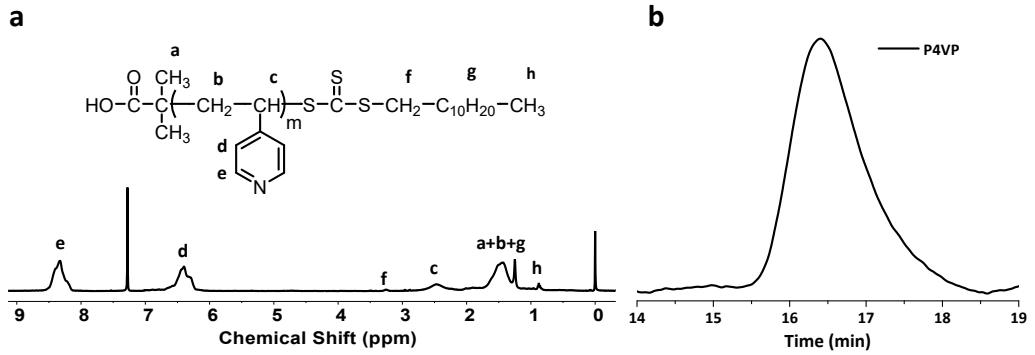


Figure S2. (a) ^{1}H NMR spectra of $P4VP_{75}$ in $CDCl_3$ and (b) GPC curve of $P4VP_{75}$.

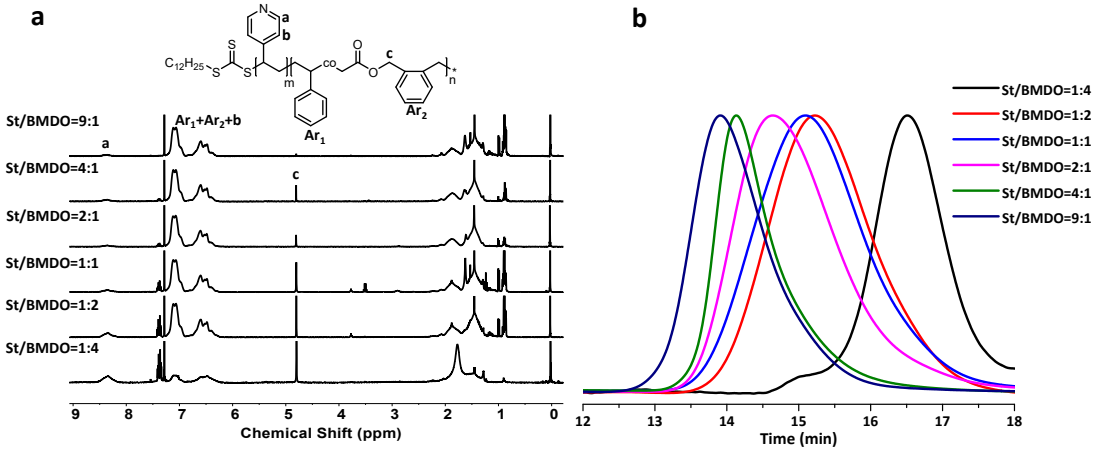


Figure S3. ^{1}H NMR spectra (a) and GPC curves (b) of copolymers with different feed ratios of St/BMDO ranged from 1:4, 1:2, 1:1, 2:1, 4:1 and 9:1. The rROPISA was performed in methanol and (St+BMDO)/P4VP = 5000.

Table S1. The characteristics and morphologies of P4VP-*b*-P(BMDO-*co*-St) prepared via rROPISA at different St/BMDO feed ratios with (St + BMDO)/P4VP = 5000.

Samples[a]	n_{St}: n_{BMDO}	f_{BMDO}[a] (%)	Mn_{NMR}[a]	Mn_{GPC}[b]	Mw/Mn[b]	D[c] (nm)	Morphology
$\mathbf{4}_{75}\mathbf{B}_{48}\mathbf{S}_{28}$	1:4	63.0	19 k	20 k	1.08	/	/
$\mathbf{4}_{75}\mathbf{B}_{47}\mathbf{S}_{430}$	1:2	9.85	60 k	45 k	1.22	135	spheres
$\mathbf{4}_{75}\mathbf{B}_{58}\mathbf{S}_{762}$	1:1	7.12	97 k	48 k	1.28	300-520	Irregular spheres
$\mathbf{4}_{75}\mathbf{B}_{33}\mathbf{S}_{850}$	2:1	3.74	102k	66 k	1.32	110-810	spheres
$\mathbf{4}_{75}\mathbf{B}_{19}\mathbf{S}_{996}$	4:1	1.87	115 k	100 k	1.14	3500	vesicles
$\mathbf{4}_{75}\mathbf{B}_{20}\mathbf{S}_{1172}$	9:1	1.64	133 k	102 k	1.18	950	vesicles

[a] As determined by ^{1}H NMR spectroscopy in $CDCl_3$. [b] Molecular weight of copolymer, as determined by GPC in DMF at 50 °C. [a] As determined by SEM images.

Table S2. Characteristics of P4VP-*b*-P(BMDO-*co*-St) and their morphologies prepared by rROPISA at different feed ratios of (St+BMDO)/P4VP with St/BMDO = 1:2.

Samples[a]	$n_{St+BMDO}$:n_{P4VP}	f_{BMDO}[a] (%)	Mn_{NMR}[a]	Mn_{GPC}[b]	Mw/Mn[b]	D[c] (nm)	Morphology
$\mathbf{4}_{75}\mathbf{B}_{151}\mathbf{S}_{30}$	1000	83.5	36 k	28 k	1.21	/	/
$\mathbf{4}_{75}\mathbf{B}_{152}\mathbf{S}_{105}$	2000	59.1	44 k	32 k	1.24	90	spheres
$\mathbf{4}_{75}\mathbf{B}_{178}\mathbf{S}_{225}$	3000	44.1	60 k	34 k	1.24	125	spheres
$\mathbf{4}_{75}\mathbf{B}_{47}\mathbf{S}_{430}$	5000	9.85	60 k	45 k	1.22	135	spheres
$\mathbf{4}_{75}\mathbf{B}_{45}\mathbf{S}_{481}$	7500	8.56	65 k	52 k	1.24	140	spheres
$\mathbf{4}_{75}\mathbf{B}_{37}\mathbf{S}_{453}$	10000	7.51	61 k	53 k	1.14	150	spheres
$\mathbf{4}_{75}\mathbf{B}_{14}\mathbf{S}_{567}$	15000	2.45	69 k	59 k	1.24	160	spheres

[a] As determined by ^{1}H NMR spectroscopy in $CDCl_3$. [b] Molecular weight of copolymer, as determined by GPC in DMF at 50 °C. [a] As determined by SEM images.

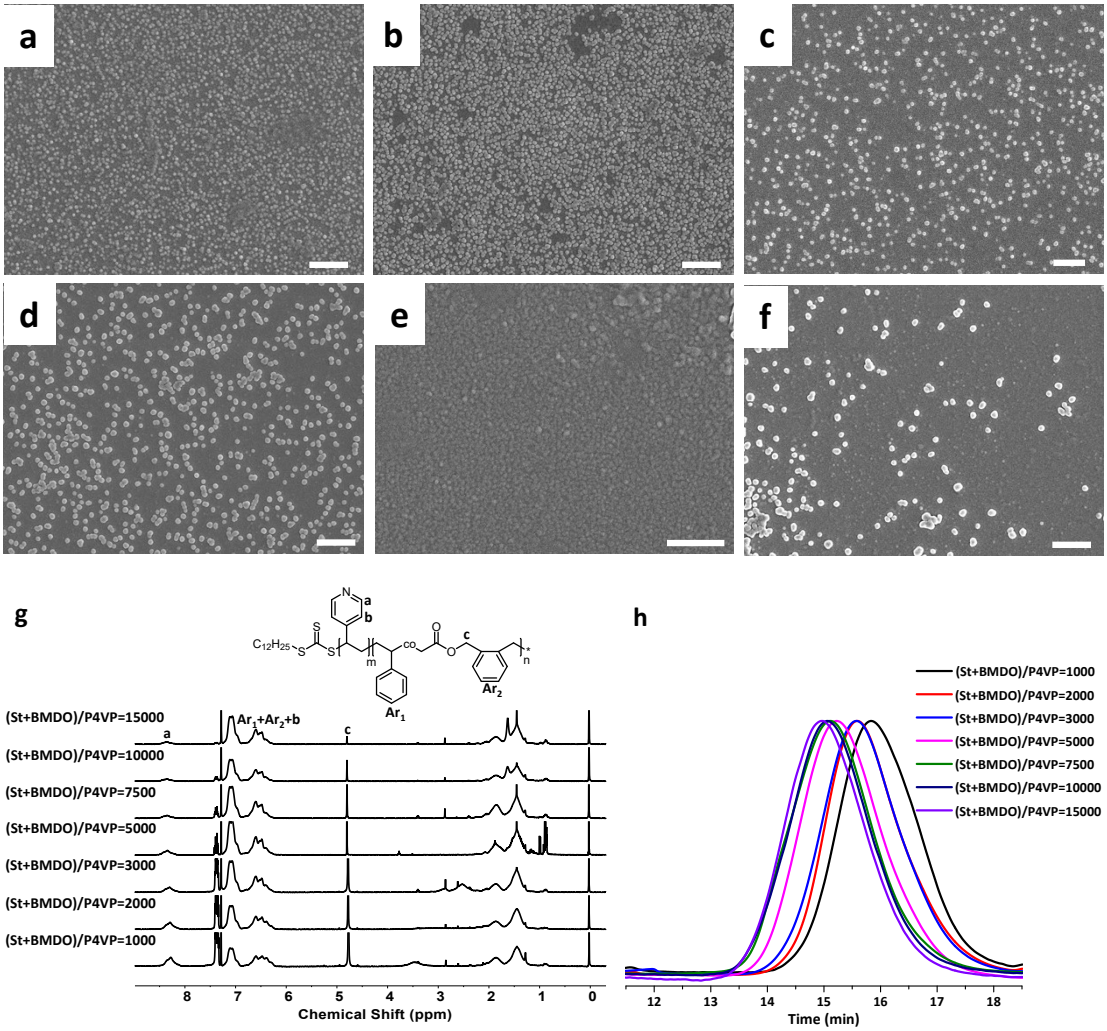


Figure S4. Morphologies of P4VP-*b*-P(St-*co*-BMDO) aggregates formed by rROPISA in methanol with the feed ratio of St/BMDO = 1:2, depending on the feed ratio of (St+BMDO)/P4VP: a for 2000 ($\mathbf{4}_{75}\mathbf{B}_{152}\mathbf{S}_{105}$, f_{BMDO} = 59.1%), b for 3000 ($\mathbf{4}_{75}\mathbf{B}_{178}\mathbf{S}_{225}$, f_{BMDO} = 44.1%), c for 5000 ($\mathbf{4}_{75}\mathbf{B}_{47}\mathbf{S}_{430}$, f_{BMDO} = 9.85%), d for 7500 ($\mathbf{4}_{75}\mathbf{B}_{45}\mathbf{S}_{481}$, f_{BMDO} = 8.56%), e for 10000 ($\mathbf{4}_{75}\mathbf{B}_{37}\mathbf{S}_{453}$, f_{BMDO} = 7.51%), f for 15000 ($\mathbf{4}_{75}\mathbf{B}_{14}\mathbf{S}_{567}$, f_{BMDO} = 2.45%). g is ^{1}H NMR spectra of copolymers with St/BMDO = 1:2 in $CDCl_3$ and h is GPC analysis of copolymers with St/BMDO=1:2 in DMF. Scale bar is 1 μm.

Table S3. Characteristics of P4VP-*b*-P(BMDO-*co*-St) and their morphologies prepared by rROPISA at different feed ratios of (St+BMDO)/P4VP with St/BMDO = 4:1.

Samples[a]	$n_{St+BMDO}$: n_{P4VP}	f_{BMDO}[a] (%)	Mn_{NMR}[a]	Mn_{GPC}[b]	Mw/Mn[b]	D[c] (nm)	Morphology
$\mathbf{4}_{75}\mathbf{B}_{40}\mathbf{S}_{258}$	1000	13.3	41k	26 k	1.23	62	spheres
$\mathbf{4}_{75}\mathbf{B}_{26}\mathbf{S}_{374}$	2000	6.39	51k	38 k	1.24	70	spheres
$\mathbf{4}_{75}\mathbf{B}_{20}\mathbf{S}_{726}$	3000	2.71	87k	78 k	1.17	120	spheres
$\mathbf{4}_{75}\mathbf{B}_{19}\mathbf{S}_{996}$	5000	1.87	115k	100 k	1.14	3500	vesicles
$\mathbf{4}_{75}\mathbf{B}_{10}\mathbf{S}_{1023}$	7500	0.94	116k	123 k	1.17	167	worms
$\mathbf{4}_{75}\mathbf{B}_{8}\mathbf{S}_{1484}$	10000	0.54	163k	141 k	1.18	2050	vesicles
$\mathbf{4}_{75}\mathbf{B}_{1}\mathbf{S}_{1962}$	15000	0.04	212k	167 k	1.17	1300	LCVs

[a] As determined by ^{1}H NMR spectroscopy in $CDCl_3$. [b] Molecular weight of copolymer, as determined by GPC in DMF at 50 °C. [a] As determined by SEM images.

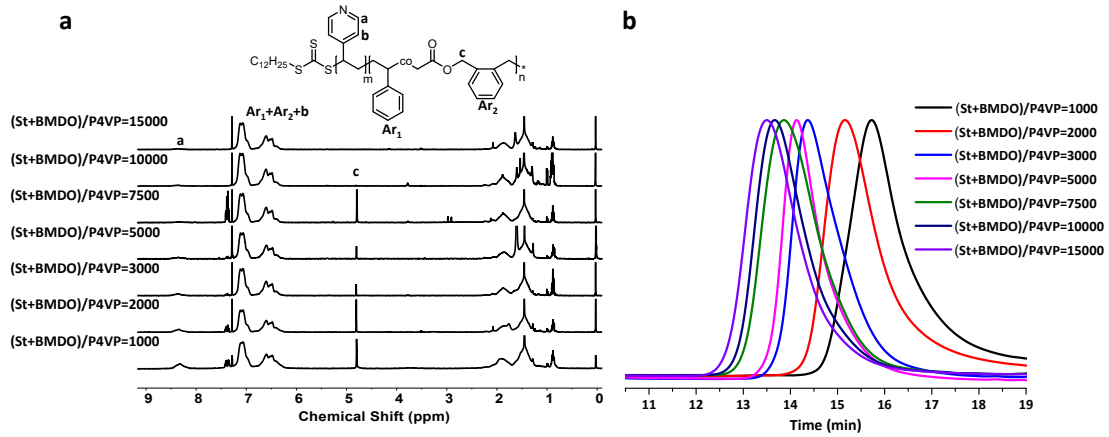


Figure S5. ^{1}H NMR spectra(a) and GPC curves (b) of copolymers with different feed ratios of (St+BMDO)/P4VP ranged from 1000, 2000, 3000, 5000, 7500,10000 and 15000. The rROPISA was performed in methanol and St/BMDO = 4:1.

Table S4. Characteristics of P4VP-*b*-P(BMDO-*co*-St) and their morphologies prepared by rROPISA at different feed ratios of (St+BMDO)/P4VP with St/BMDO = 9:1.

Samples[a]	$n_{St+BMDO}$:n_{P4VP}	f_{BMDO}[a] (%)	Mn_{NMR}[a]	Mn_{GPC}[b]	Mw/Mn[b]	D[c] (nm)	Morphology
$\mathbf{4}_{75}\mathbf{B}_{18}\mathbf{S}_{397}$	1000	4.34	52 k	37 k	1.16	65	spheres
$\mathbf{4}_{75}\mathbf{B}_{24}\mathbf{S}_{586}$	2000	3.93	73 k	75 k	1.15	115	spheres
$\mathbf{4}_{75}\mathbf{B}_{26}\mathbf{S}_{671}$	3000	3.66	82 k	75 k	1.18	220	spheres
$\mathbf{4}_{75}\mathbf{B}_{20}\mathbf{S}_{1172}$	5000	1.64	133 k	102 k	1.20	1170	vesicles
$\mathbf{4}_{75}\mathbf{B}_{17}\mathbf{S}_{1689}$	7500	1.01	186 k	112 k	1.26	1219	vesicles
$\mathbf{4}_{75}\mathbf{B}_{12}\mathbf{S}_{2103}$	10000	0.57	229 k	131 k	1.33	3560	LCVs
$\mathbf{4}_{75}\mathbf{B}_{0}\mathbf{S}_{5804}$	15000	0.00	612 k	172 k	1.23	4417	LCVs

[a] As determined by ^{1}H NMR spectroscopy in $CDCl_3$. [b] Molecular weight of copolymer, as determined by GPC in DMF at 50 °C. [a] As determined by SEM images.

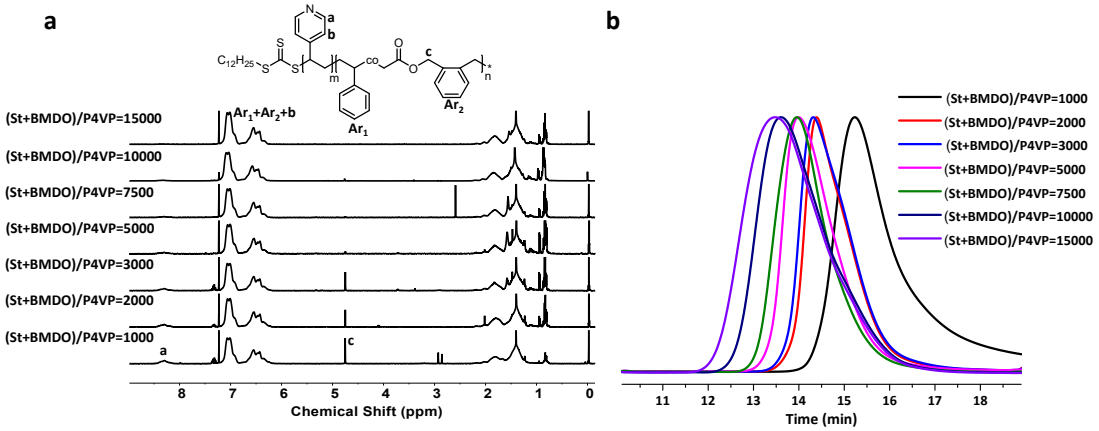


Figure S6. ^{1}H NMR spectra(a) and GPC curves (b) of copolymers with different feed ratios of (St+BMDO)/P4VP ranged from 1000, 2000, 3000, 5000, 7500,10000 and 15000. The rROPISA was performed in methanol and St/BMDO = 9:1.

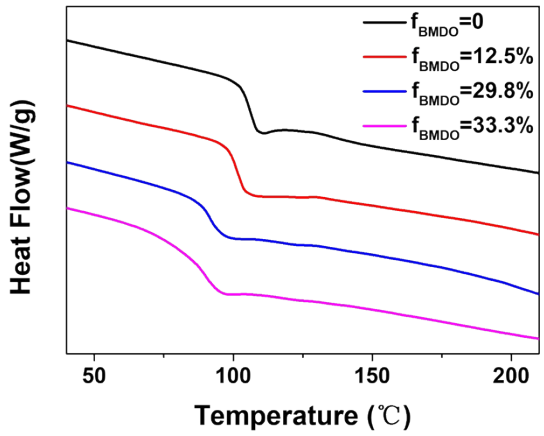


Figure S7. DSC curves of copolymers with different BMDO content.

Table S5. Characteristics of copolymers with different BMDO content.

Samples [a]	F_{BMDO} [b]	f_{BMDO} [a]	T_g (°C) [c]
P4VP$_{75}$-*b*-PS$_{560}$	0	0	106.34
P4VP$_{75}$-*b*-P(BMDO$_{40}$-*co*-St$_{258}$)	20%	12.5%	101.06
P4VP$_{75}$-*b*-P(BMDO$_{368}$-*co*-St$_{868}$)	80%	29.8%	94.72
P4VP$_{75}$-*b*-P(BMDO$_{113}$-*co*-St$_{225}$)	80%	33.3%	90.22

[a] As determined by ^{1}H NMR spectroscopy ($CDCl_3$). [b] The feeding content of BMDO. [c] As measured by DSC.

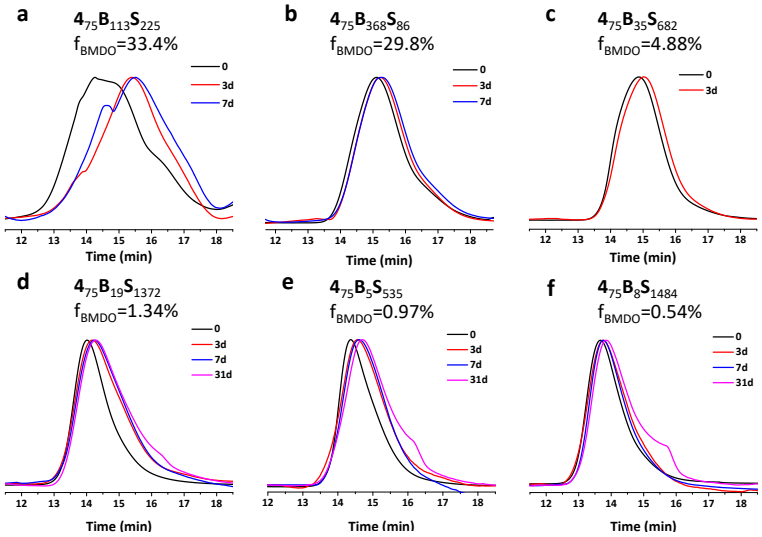


Figure S8. GPC curves of copolymers with different f_{BMDO} before and after the degradation.

Table S6. Characteristics of copolymers before and after the degradation

Samples[a]	F_{BMDO}[b]	f_{BMDO}[a]	*Mn*(g/mol) before degradation[c]	*Mn*(g/mol) after degradation[c]		
				3 days	7 days	31days
$4_{75}B_{113}S_{225}$	80%	33.4%	54.8 k	38.4 k	35.3 k	30.1k
$4_{75}B_{368}S_{868}$	80%	29.8%	58.6 k	46.6 k	45.3 k	32.5k
$4_{75}B_{19}S_{1372}$	20%	1.34%	99.6 k	94.2 k	87.6 k	57.0k
$4_{75}B_{5}S_{535}$	20%	0.97%	78.0 k	74.9 k	72.4 k	52.9k
$4_{75}B_{8}S_{1484}$	20%	0.54%	140.7 k	139.6 k	137.4 k	106.3k

[a] As determined by ^{1}H NMR spectroscopy in $CDCl_3$. [b] The feeding content of BMDO. [c] Molecular weight decrease of copolymer, as determined by GPC in DMF at 50°C.

5. References

1 J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.