Photoluminescent polymer cubosomes prepared by

RAFT-mediated polymerization-induced self-assembly

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Additional Experimental Procedures.

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl acrylate (TBA). 4-(Hydroxymethyl)phenylboronic acid pinacol ester (10.0 g, 42.7 mmol, 1.0 equiv.) and acrylic acid (4.6 g, 64.1 mmol, 1.5 equiv.) were dissolved in 80.0 mL dichloromethane under argon atmosphere in a round bottom flask equipped with a magnetic stirring bar. Next, DIC (8.1 g, 64.1 mmol, 1.5 equiv.) and DMAP (1.0 g, 8.5 mmol, 0.2 equiv.) were added in sequence. The reaction mixture was stirred at room temperature for 16 hours, the formed precipitate was removed by gravity filtration. The obtained solution was diluted with extra 200 mL dichloromethane and washed with 1M HCl (100 mL \times 3) solution and saturated sodium chloride solution (100 mL \times 1), respectively. The organic layer was then dried over anhydrous MgSO4 and concentrated by using a rotary evaporator. The product was purified by silica gel column chromatography with hexane and ethyl acetate (5:1, v/v) as eluent to yield a white solid (7.0 g, 57%). ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J*=7.83 Hz, 2H), 7.37 (d, *J*=7.83 Hz, 2H), 6.42 (dd, *J*=1.47, 17.12Hz, 1H), 6.18 (dd, J=10.27, 17.12 Hz, 1H), 5.86 (dd, J=1.47, 10.27 Hz, 1H), 5.21 (s, 2H), 1.34 (s, 12H).

Synthesis of (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (TPE). Tetrabutylammonium tribromide (574.0 mg, 1.2 mmol, 0.1 equiv.) was dissolved in a mixture composed of 100 mL toluene and 24 mL potassium carbonate aqueous solution (2 M) in a 500 mL round bottom flask equipped with a magnetic stirring bar. Next, 2-bromo-1,1,2-triphenylethylene (4.0 g, 11.9 mmol, 1.0 equiv.) and 4-vinylphenylboronic acid (2.7 g, 17.9 mmol, 1.5 equiv.) were added in sequence. The reaction mixture was stirred at room temperature for a half-hour under argon, tetrakis(triphenylphosphine)palladium(0) (20 mg) was then added to the mixture. After it has been stirred at 85 °C for 24 hours, the suspension was cooled down to room temperature and extracted with a mixture of 400 mL dichloromethane and 200 mL water. The organic layer was then dried over anhydrous MgSO4 and concentrated by using a rotary evaporator. The product was purified by silica gel column chromatography with hexane and dichloromethane (5:1, v/v) as eluent to yield a white solid (3.5 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ

6.97-7.24 (m, 19H), 6.60 (dd, *J*=17.6 Hz, 10.8 Hz, 1H), 5.66 (dd, *J*=17.6 Hz, 1.0 Hz, 1H), 5.21 (dd, *J*=10.8 Hz, 1.0 Hz, 1H).

Additional Figures.



Figure S1. ¹H NMR spectrum of the monomer TBA (CDCl₃, 400 MHz).



Figure S2. ¹H NMR spectrum of the monomer TPE (CDCl₃, 400 MHz).



Figure S3. ¹H NMR spectrum of PDMA₄₁-CDPA (CDCl₃, 400 MHz). *The number of the repeating units was calculated by comparing the integration of peak f and peak c+b, which equals (Integration of peak c+b)*/7=287/7=41.



Figure S4. Representative ¹H NMR spectra of the PISA crude solution at 15% w/w solid content with AIBN as initiator at 65 °C (CDCl₃, 400 MHz) with target DP of 250, (up) 0% of TPE monomer, (down) 5 mol% of TPE monomer. With the presence of 5 mol% TPE monomer, a large amount of TBA monomers were not converted into PTBA, however, all TPE monomers were converted into PTPE.



Figure S5. ¹H NMR spectra of the PISA crude solution at different reaction timeframes, 15% w/w solid content with AIBN as initiator at 65 °C (CDCl₃, 400 MHz) with target DP of 250 and 5 mol% of TPE monomer. *It has been noticed that the TPE monomers were all consumed in the first few hours of the reaction, and the TBA monomers polymerized at the later stage of the reaction. Due to the small amount of TPE monomer observed in the spectra, the integrations of TPE and PTPE peaks are not accurate and, therefore, are not labelled.*



Figure S6. SEC traces of the diblock copolymer PDMA₄₁-*b*-PTBA_x at 15% w/w solid content. (DMF as solvent, PS standards). *PDMA₄₁* ($M_n = 5.4$ kg/mol, D = 1.06, *PMMA standards*).

Table S1.	. Characterization	data of PDMA ₄₁ -b-	PTBA _x di-block	copolymers s	synthesized in	methanol at	15%
w/w solid	content. ^[a]						

Entry	Macro- RAFT / TBA ratio	Conversion (%) ^[b]	Composition	M _{n,theo} . ^[c] (kg/mol)	M _{n,SEC} ^[d] (kg/mol)	Ð	Morphology
1	1:60	>99.0	PDMA ₄₁ - <i>b</i> -PTBA ₆₀	21.8	30.9	1.21	Spherical micelle
2	1:90	>99.0	PDMA ₄₁ - <i>b</i> -PTBA ₉₀	30.4	41.0	1.23	Worm + Jellyfish
3	1:150	91.7	PDMA45-b-PTBA138	44.2	60.1	1.23	Vesicle
4	1:200	90.9	PDMA45-b-PTBA182	56.9	76.0	1.25	Vesicle + compound vesicle
5	1:250	92.2	PDMA45-b-PTBA231	71.0	83.7	1.40	Vesicle + compound vesicle + spongosome
6	1:260	89.7	PDMA45-b-PTBA234	71.9	89.2	1.38	Spongosome + <i>cubosome</i>
7	1:270	90.6	PDMA45-b-PTBA245	75.1	88.4	1.46	cubosome
8	1:280	90.0	PDMA45-b-PTBA252	77.1	96.5	1.45	Solid particle

[a]: All polymerizations were conducted at 15 wt% solid content, 65 °C, with AIBN as initiator.

[b]: Conversion was determined by comparing the peak integrations between monomer and polymer in the ¹H NMR spectrum of crude solution after PISA process.

[c]: Theoretical molecular weight of the copolymers= $(41 \times M_{DMA}) + M_{CDPA} + (DP_{(PTBA)} \times M_{TBA})$.

[d]: Molecular weight of copolymers as determined by DMF SEC relative to PS standards. PS standards are used to calibrate the block copolymers as the obtained relative values are closer to polymer theoretical molecular weights.



Figure S7. Transmission electron microscopy (TEM) micrographs of the PDMA₄₁-*b*-PTBA_x diblock copolymer nanoobjects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) x = 60, b) x = 90, c) x = 138, d) x = 182, e) x = 231, f) x = 234, g) x = 245, h) x = 252.



Figure S8. Scanning electron microscopy (SEM) micrographs of the PDMA₄₁-*b*-PTBA_x diblock copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) and b) x = 234, c) and d) x = 245.



Figure S9. SAXS profile of the PDMA₄₁-*b*-PTBA₂₄₅ diblock copolymer cubosome. *The lattice constant a* = 45.5 nm.



Figure S10. The profile of TBA monomer conversions *vs* target DP under the PISA processes with different percentages of TPE.



Figure S11. SEC traces of the block copolymer $PDMA_{41}$ -*b*-P(TBA-*r*-TPE)_x at 15% w/w solid content, the addition ratio of TPE was 5 mol% of total monomers. (DMF as the solvent, PS standards).

Table S2. Characterization data of PDMA₄₁-*b*-P(TBA-*r*-TPE)_x block copolymers synthesized in methanol at 15% w/w solid content, the addition ratio of TPE was 5 mol% of total monomers. ^[a]

Entry	Macro-RAFT / TBA/TPE ratio	Conversion	Composition	M _{n,theo} . ^[c] (kg/mol)	$M_{n,SEC}^{[d]}$ (kg/mol)	Ð	Morphology
1	1: 85.5: 4.5	72.1	PDMA ₄₁ - <i>b</i> -PTBA ₆₂ -PTPE ₅	24.1	30.1	1.21	Spherical micelle
2	1:190: 10	51.7	PDMA41-b-PTBA98-PTPE10	36.3	42.5	1.23	Phase-separated worm
3	1:285: 15	47.9	PDMA41-b-PTBA137-PTPE15	49.3	52.7	1.28	Phase-separated vesicle
4	1:332.5: 17.5	44.1	PDMA41-b-PTBA147-PTPE18	53.3	58.3	1.33	Phase-separated vesicle
5	1:323: 17	52.6	PDMA41-b-PTBA170-PTPE17	59.6	68.5	1.39	Vesicle + compound
							vesicle + spongosome
6	1:361: 19	59.0	PDMA41-b-PTBA213-PTPE19	72.7	74.1	1.55	Spongosome + solid
							particle

[a]: All polymerizations were conducted at 15 wt% solid content, 65 °C, with AIBN as initiator.

[b]: Conversion was determined by comparing the peak integrations between monomer and polymer in the ¹H NMR spectrum of crude solution after the PISA process.

[c]: Theoretical molecular weight of the copolymers= $(41 \times M_{DMA}) + M_{CDPA} + (DP_{(PTBA)} \times M_{TBA} + DP_{(PTPE)} \times M_{TPE}).)$

[d]: Molecular weight of copolymers as determined by DMF SEC relative to PS standards.



Figure S12. Transmission electron microscopy (TEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 5 mol% of total monomers) block copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) x = 66, b) x = 86, c) x = 152, d) x = 165, e) x = 187, f) x = 232.



Figure S13. Scanning electron microscopy (SEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 5 mol% of total monomers) block copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) and b) x = 165, c) and d) x = 187, e) and f) x = 232.



Figure S14. SAXS profile of the PDMA₄₁-*b*-PTBA₂₁₃-PTPE₁₉ or PDMA₄₁-*b*-P(TBA-*r*-TPE)₂₃₂ block copolymer particles. *No distinctive scattering peaks were observed.*



Figure S15. SEC traces of the block copolymer $PDMA_{41}$ -*b*-P(TBA-*r*-TPE)_x at 15% w/w solid content, the addition ratio of TPE was 2 mol% of total monomers. (DMF as the solvent, PS standards).

Table S3. Characterization data of PDMA ₄₁ - <i>b</i> -P(TBA- <i>r</i> -TPE) _x block copolymers	synthesized	in methanol at	ŧ
15% w/w solid content, the addition ratio of TPE was 2 mol% of total monomers.	[a]		

Entry	Macro-RAFT /	Conversion	Composition	Mn,theo. ^[C]	Mn,SEC ^[d]	Ð	Morphology
	TBA/TPE ratio	(%) ^[b]		(kg/mol)	(kg/mol)		
1	1: 58.8: 1.2	>99.0	PDMA41-b-PTBA59-PTPE1	21.8	30.2	1.22	Spherical micelle
2	1:88.2: 1.8	92.2	PDMA41-b-PTBA81-PTPE2	28.5	37.5	1.25	Worm + Jellyfish
3	1:147: 3	80.0	PDMA41-b-PTBA118-PTPE3	39.6	45.2	1.25	Vesicle
4	1:196:4	78.1	PDMA ₄₁ - <i>b</i> -PTBA ₁₅₃ -PTPE ₄	50.0	65.6	1.26	Vesicle + compound
							vesicle
5	1:245: 5	84.5	PDMA41-b-PTBA207-PTPE5	65.9	76.9	1.36	Spongosome

6	1:254.8: 5.2	85.6	PDMA41-b-PTBA218-PTPE5	69.1-	78.4	1.43	Spongosome +
							cubosome
7	1:269.5: 5.5	83.1	PDMA ₄₁ - <i>b</i> -PTBA ₂₂₄ -PTPE ₆	71.2	70.0	1.40	Cubosome
8	1:279.3: 5.7	82.0	PDMA ₄₁ -b-PTBA ₂₂₉ -PTPE ₆	72.6	74.1	1.37	Cubosome + solid
							particle
9	1:259.7: 5.3	92.6	PDMA ₄₁ -b-PTBA ₂₄₅ -PTPE ₅	76.9	82.3	1.50	Cubosome + hexosome+
							solid particle

[a]: All polymerizations were conducted at 15 wt% solid content, 65 °C, with AIBN as initiator.

[b]: Conversion was determined by comparing the peak integrations between monomer and polymer in the ¹H NMR spectrum of crude solution after PISA process.

[c]: Theoretical molecular weight of the copolymers= $(41 \times M_{DMA}) + M_{CDPA} + (DP_{(PTBA)} \times M_{TBA} + DP_{(PTPE)} \times M_{TPE}).)$

[d]: Molecular weight of copolymers as determined by DMF SEC relative to PS standards.



Figure S16. Scanning electron microscopy (SEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 2 mol% of total monomers) block copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) x = 60, b) x = 83, c) x = 121, d) x = 157, e) x = 223, f) x = 235.



Figure S17. Additional transmission electron microscopy (TEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 2 mol% of total monomers) block copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) x = 74, b) x = 83, c) x = 88. *These images show the morphological evolution from worm-like micelles to jellyfish-like structures, and vesicles.*



Figure S18. SAXS profile of the PDMA₄₁-*b*-PTBA₂₂₉-PTPE₆ or PDMA₄₁-*b*-P(TBA-*r*-TPE)₂₃₅ block copolymer particles.



Figure S19. Additional transmission electron microscopy (TEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 2 mol% of total monomers) block copolymer micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 20% w/w solid content and 65 °C. a) x = 235, b), c) x = 240.



Figure S20. SEC traces of the block copolymer $PDMA_{41}$ -*b*-P(TBA-*r*-TPE)_x at 15% w/w solid content, the addition ratio of TPE was 1 mol% of total monomers. (DMF as the solvent, PS standards).

Table S4. Characterization data of PDMA₄₁-*b*-P(TBA-*r*-TPE)_x block copolymers synthesized in methanol at 15% w/w solid content, the addition ratio of TPE was 1 mol% of total monomers. ^[a]

Entry	Macro-RAFT / TBA/TPE ratio	Conversion (%) ^[b]	Composition	M _{n,theo} . ^[c] (kg/mol)	M _{n,SEC} ^[d] (kg/mol)	Ð	Morphology
1	1: 59.4: 0.6	>99.0	PDMA ₄₁ - <i>b</i> -PTBA ₅₉ -PTPE ₁	21.8	38.1	1.22	Spherical micelle
2	1:89.1: 0.9	95.2	PDMA ₄₁ - <i>b</i> -PTBA ₈₅ -PTPE ₁	29.3	42.5	1.21	Worm + Jellyfish

3	1:148.5: 1.5	89.5	PDMA ₄₁ - <i>b</i> -PTBA ₁₃₃ -PTPE ₂	43.5	53.7	1.33	Vesicle
4	1:198: 2	90.7	PDMA ₄₁ - <i>b</i> -PTBA ₁₈₀ -PTPE ₂	57.1	75.8	1.29	Vesicle + compound
							vesicle
5	1:247.5: 2.5	90.1	PDMA ₄₁ - <i>b</i> -PTBA ₂₂₃ -PTPE ₃	69.8	87.5	1.40	Spongosome
6	1:257.4: 2.6	87.8	PDMA ₄₁ - <i>b</i> -PTBA ₂₂₆ -PTPE ₃	70.7	83.1	1.26	Spongosome +
							cubosome
7	1:257.4: 2.6	92.1	PDMA41-b-PTBA237-PTPE3	73.8	87.5	1.52	Cubosome
8	1:267.3: 2.7	90.1	PDMA ₄₁ -b-PTBA ₂₄₃ -PTPE ₃	75.6	89.2	1.48	Cubosome + solid
							particle

[a]: All polymerizations were conducted at 15 wt% solid content, 65 °C, with AIBN as initiator.

[b]: Conversion was determined by comparing the peak integrations between monomer and polymer in the ¹H NMR spectrum of crude solution after PISA process.

[c]: Theoretical molecular weight of the copolymers= $(41 \times M_{DMA}) + M_{CDPA} + (DP_{(PTBA)} \times M_{TBA} + DP_{(PTPE)} \times M_{TPE}).)$

[d]: Molecular weight of copolymers as determined by DMF SEC relative to PS standards.



Figure S21. Transmission electron microscopy (TEM) micrographs of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 1 mol% of total monomers) block copolymer nano-objects or micro-objects prepared by polymerization-induced self-assembly (PISA) in methanol at 15% w/w solid content and 65 °C. a) x = 60, b) x = 86, c) x = 134, d) x = 182, e) x = 226, f) x = 229, g) x = 240, h) x = 246.



Figure S22. SAXS profile of the PDMA₄₁-*b*-PTBA₂₃₇-PTPE₃ or PDMA₄₁-*b*-P(TBA-*r*-TPE)₂₄₀ block copolymer particles. *The particle lattice constant a* = 45.2 nm.



8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 Chemical Shift (ppm)

Figure S23. ¹H NMR spectra (CDCl₃, 400 MHz) comparison of PISA particle suspension before and after dialysis in methanol. The particles were composed of PDMA₄₁-*b*-P(TBA-*r*-TPE)₁₅₇ (the addition ratio of TPE was 2 mol% of total monomers). *It has been observed that the residual TBA monomers were completely removed by the dialysis process.*



Figure S24. ¹H NMR spectra (CDCl₃, 400 MHz) comparison of PISA particle suspension before and after dialysis in methanol. The particles were composed of PDMA₄₁-*b*-P(TBA-*r*-TPE)₂₃₀ (the addition ratio of TPE was 2 mol% of total monomers). *It has been observed that the residual TBA monomers were completely removed by the dialysis process.*



Figure S25. Transmission electron microscopy (TEM) micrographs comparison of the PDMA₄₁-*b*-P(TBA-*r*-TPE)_x (the addition ratio of TPE was 2 mol% of total monomers) block copolymer nano-objects or micro-objects before and after dialysis in methanol. a) and b) x = 157, c) and d) x = 230. *It was observed that the dialysis process did not cause obvious morphological changes in particles.*



Figure S26. CLSM images of cubosomes with 0% TPE taken under a) bright field and b) irradiated at 405 nm and collected at 425-475 nm.



Figure S27. a) Fluorescence spectra of polymer cubosomes with the incorporation of 2-0.1 mol% of TPE, b) photograph of these cubosomes under UV light of 365 nm.



Figure S28. a) Fluorescence spectra of polymer nano/micro-objects with incorporation of 2 mol% of TPE, b) photograph of these nano/micro-objects under UV light of 365 nm, micelle (M), worm (W), vesicle (V), spongosome (S), cubosome (C).



Figure S29. Fluorescence spectra of polymer a) cubosomes and c) vesicles (1.5 mg/mL in methanol) with/without the addition of 100 mM H_2O_2 after 16-hour incubation at 40 °C; b) photograph of cubosomes and vesicles suspension in methanol with/without the addition of H_2O_2 under UV light of 365 nm.