Electronic Supplementary Material (ESI) for Polymer Chemistry.

Multipath Aerobic-Mediated PET-RAFT Polymerization by Conjugated Organic Polymers Photocatalyst under Red LED Irradiation

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1. Materials

Most of the chemicals were purchased from commercial sources. Methyl methacrylate (MMA, 99%), benzyl methacrylate (BzMA, 99%), glycidyl methacrylate (GMA, 97%), N-(2-hydroxylpropyl) methacrylamide (HPMA, 97%), 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%), 2-Methoxyethyl methacrylatewas (MEMA, 99%) purchased from Sigma-Aldrich and the inhibitor was removed by passing through a neutral alumina column. 4-Cyano-4-(thiobenzoylthio)pentanoic acid (CPADB) was purchased from Aladdin (China) and was used as received. N-N-Dimethylacetamide (DMAc, AR), triethylamine (TEA, 99.8%), triethanolamine (TEOA, 99.8%), N,N,N',N",N"'-Pentamethyldiethylenetriamine (PMDETA, 99%), n-Butanol (99.8%), 1,2-dichlorobenzene (99.8%), acetic acid (98%), methol (MeOH, AR), tetrahydrofuran (THF, AR), acetone (AR) were were all purchased from Sigma-Aldrich. Tetra(p-amino-phenyl)porphyrin[S1,S2] (TAPP) was synthesized using published procedures. All other reagents were used as received unless otherwise specified.

RED light-emitting diode flex strip (13 W m^{-1}, 15 mW cm^{-2}) was used as an LED red source.

2. Characterization

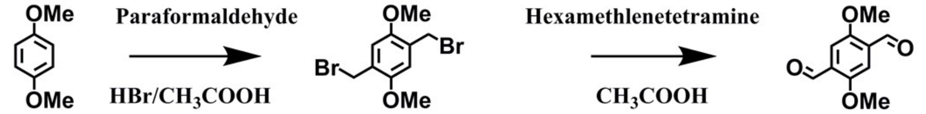
^{1}H NMR (600 MHz) spectra were recorded on Bruker Advance III. The UV-vis spectra were recorded on Genesys 10S Uv-vis spectrophotometer (Thermal Fisher Scientific).. Powder X-ray diffraction (PXRD) studies were performed on EmpyreanDY1602. The specific surface areas and pore size distributions of product were investigated on an Autosorb-iQ analyzer (Quantachrome).

3. Gel Permeation Chromatography (GPC)

Number-average molecular weight (M_n) and dispersities (M_w/M_n) of obtained polymers were measured by GPC with refractive index detector (Waters, 2414), using THF as eluent with three Phenomenex phenogel columns (500, 104, 106 Å porosity 5μm bead size) at a flow rate of 1.00 mL/min (40 °C). All samples were filtered through 0.45 μm nylon filters prior to injection. THF GPC was calibrated based on narrow molecular weight distribution of PMMA standards with molecular weights of 2230 to 96100 g mol^{-1}.

4. Synthesis procedure

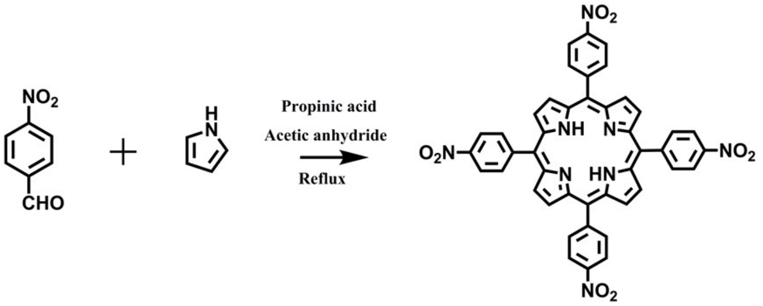
4.1. Synthesis of 2,5-dimethoxyterephthalaldehyde (DMTA):



DMTA was prepared according to the previous literature. 1,4-Dimenthoxybenzene (8.28 g, 0.06 mol) and paraformaldehyde (8.10 g, 0.27 mol) was dissolved in glacial acetic acid (60 mL) and then hydrobromic acid (33 wt%) in acetic acid solution (30 mL) were added dropwise. The mixture was stirred at 70 °C for 6 h. After cooled to room temperature, the mixture was poured into the ice water and the precipitate was filtered and washed several times with water to afford white 4-bis(bromomethyl)-2,5-dimethoxybenzene with 92% yield (17.88 g).

1,4-Bis(bromomethyl)-2,5-dimethoxybenzene (9.72 g, 0.03 mol) and hexamethylenetetramine (12.60 g, 0.09 mol) was suspended in anhydrous chloroform (200 mL) and refluxed at 70 °C for 10 h. The solvent was evaporated under reduced pressure and then 50% acetic acid (100 ml) was added. The mixture was continued to be refluxed at 120 °C for 24 h, subsequently the concentrated hydrochloric acid (4 mL) was added and refluxed at 120 °C for 4h. After cooled to room temperature, the mixture was extracted by CH_2Cl_2, dried by anhydrous magnesium sulfate. The solvent was evaporated, and the precipitate was purified by column chromatography in ethyl acetate and dichloromethane (50% v/v) to give pale yellow powder of DMTA with 26% yield (1.52 g). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.92 (s, 8H), 8.01 (d, J = 8.2 Hz, 8H), 7.09 (d, J = 8.2 Hz, 8H), 4.05 (s, 8H), -2.69 (s, 2H).

4.2. Synthesis of 5,10,15,20-Tetrakis(4-aminophenyl)-porphyrin(TCPP):



4-nitrobenzaldehyde (22.0 g, 145 mmol), Propionic acid (600 mL) and acetic anhydride (24 mL) were added into flask (1000 mL) and the mixture was refluxed at 145 °C under nitrogen atmosphere. Subsequently, Pyrrole (10 mL) was added by needle and the mixture reacted for 12 h. After cooling down to room temperature, the mixture was put into refrigerator overnight, then the solid was obtained by filtered and further washed with distilled water (200 mL) and methanol (500 mL), the product was dried under vacuum. The solid was refluxed at 120 °C in pyridine (160 mL) under nitrogen protected for 12 h. The mixture was coolled down to room temperature, the black solid was obtained by filtered, and washed with acetone to give purple solid.

The product and $SnCl_2$ 2 H_2O (18.0 g, 7.97 mmol) were further added into hot concentration hydrochloric acid (500 mL) solution for refluxing at 110 °C under nitrogen atmosphere overnight. The mixture was cooled to 0 ^{o}C with ice water and neutralized with concentrated ammonium hydroxide until pH = 8 to give green crude product. The final product, **TCPP**, was purified by recrystallization using acetone as solvent. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.90 (s, 8 H), 7.99 (s, 8H), 7.05 (s, 8H), 4.00 (s, 8H), -2.71 (s, 2H).

4.3. Synthesis of TCPP-DMTA-COP

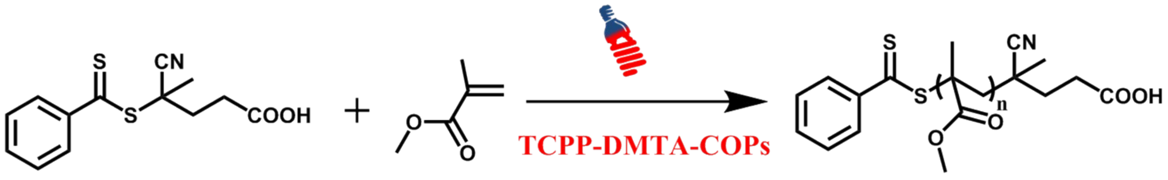
A Schlenk tube was charged with **TCPP** (14.8 mg, 0.02 mmol), **DMTA** (7.8 mg, 0.04mmol), 0.5 mL of *n*-BuOH, 0.5 mL of *o*-DCB and HAc (0.1 mL, 6M aq.). After being degassed by freeze-pump-thaw for three times and sealed under vacuum, the tube was placed in an oven at 120 ^{o}C for 7 days. The mixture was cooled down to room temperature and the black precipitate was collected and washed with THF and subjected to Soxhlet extraction with THF as solvent for 12 h and dried under vacuum at 120 ^{o}C for 2 h. The final product, **TCPP-DMTA-COP**, was afforded as black solid in 82% yield.

5. Photoelectrochemical measurements

Photoelectrochemical measurements were performed on CHI 660e electrochemical workstation with standard three-electrode electrochemical cell with a working electrode, a platinum plate as counter electrode, a saturated Ag/AgCl electrode as reference electrode and using sodium sulfate solution (0.2 M) as the electrolyte.

Working electrode prepared: 5 mg TCPP-DMTA-COP powder was mixed with 1.0 mL ethanol and 10 μL Nafio solution and sonicated for 0.5 h. Subsequently, 10 μL of mixture solution was dropped onto the surface of a FTO glass plate with 1 × 1 cm^2 area and left in the air to dry.

6. General polymerization procedure



General polymerization procedure

6.1. General procedure of TCPP-DMTA-COP-catalyzed PET-RAFT polymerization under aerobic condition.

For the polymerization of MMA (2.0 mL, 18.82 mmol, 200 equiv.), CPADB (26.3 mg, 0.0941 mmol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) and TEA (130.1 μL, 0.941 mmol, 10 equiv.) were added to a 4 mL glass cuvette (2 mm pathlength). The glass vial was sealed with threaded rubber plug without nitrogen purging step for polymerizations conducted in the presence of air. The concentrations of TEA were adjusted as necessary (i.e. CPADB:TEA = 1:0, 1:5, 1:10 and 1:20). The mixture was then irradiated with a red LED light (13 W m^{-1}, 15 mW cm^{-2}), polymerized as above for 48 hours. In addition, the solution was finally removed from the light source after irradiation and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to determine the monomer conversion, number-average molecular weights (M_n) and the dispersity (M_w/M_n).

6.2. General procedure of TCPP-DMTA-COP-catalyzed PET-RAFT polymerization under nitrogen atmosphere.

For the polymerization of MMA (2.0 mL, 18.82 mmol, 200 equiv.), CPADB (26.3 mg, 0.0941 mmol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) and TEA (130.1 μL, 0.941 mmol, 10 equiv.) were added to a 25 mL Schlenk tube, and the mixture was deoxygenized by freeze-pump-thaw for three times and the mixture was deoxygenized by freeze-pump-thaw for three times. The concentrations of TEA were adjusted as necessary (i.e. CPADB:TEA = 1:0 and 1:10). The mixture was then irradiated with a red LED light (13 W m^{-1}, 15 mW cm^{-2}), polymerized as above for 48 hours. In addition, the solution was finally removed from the light source after irradiation and analyzed by ^{1}H NMR ($CDCl_3$) and GPC (THF) to determine the conversions, number-average molecular weights (M_n) and the dispersity (M_w/M_n).

6.3. Demonstration of light-induced temporal control in TCPP-DMTA-COP-catalyzed PET-RAFT polymerization.

For the polymerization of MMA (2.0 mL, 18.82 mmol, 200 equiv.), CPADB (26.3 mg, 0.0941 mmol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) were added to a 4 mL glass cuvette (2 mm pathlength). The glass vial was sealed with threaded rubber plug without nitrogen purging step for polymerizations conducted in the presence of air. The concentrations of TEA were adjusted as necessary (i.e. CPADB:TEA = 1:0, 1:5, 1:10 and 1:20). At pre-determined reaction times, the light source was turned off and the vial left in darkness for the predetermined duration. Polymerization was reactivated by switching the light source on.

6.4. General procedure for the preparation of block copolymers by TCPP-DMTA-COP-catalyzed PET-RAFT polymerization.

A general process for synthesis **PMMA-*b*-PGMA** is shown as follow: The mixture consisting of GMA (2.0 mL, 15.12 mmol, 1000 equiv.), macro-CTA (304.0 mg, M_n = 20100 g/mol, 0.015 mol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) and TEA (21.0 μL, 0.15 mmol, 10 equiv.) were then irradiated with a red LED light (13 W m^{-1}, 15 mW cm^{-2}), polymerized as above . The polymer was purified by precipitation and subsequently analyzed by ^{1}H NMR and GPC.

A general process for synthesis **PMMA-*b*-PHPMA** is shown as follow: The mixture consisting of HPMA (2.0 mL, 14.78 mmol, 500 equiv.), macro-CTA (95.0 mg, M_n = 3200 g/mol, 0.030 mol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) and TEA (42.0 μL, 0.30 mmol, 10 equiv.) were then irradiated with a red LED light (13 W m^{-1}, 15 mW cm^{-2}), polymerized as above . The polymer was purified by precipitation and subsequently analyzed by ^{1}H NMR and GPC.

6.5. Demonstration of gas-induced temporal control in TCPP-DMTA-COP -catalyzed PET-RAFT polymerization.

For the polymerization of MMA (2.0 mL, 18.82 mmol, 200 equiv.), CPADB (26.3 mg, 0.0941 mmol, 1 equiv.), TCPP-DMTA-COP (1.0 mg), DMAc (1.0 mL) were added to a 4 mL glass cuvette (2 mm pathlength). The glass vial was sealed with threaded rubber plug without nitrogen purging step for polymerizations conducted in the presence of air. The mixture was then irradiated with a red LED light (13 W m^{-1}, 15 mW cm^{-2}), polymerized as above and analyzed by GPC (THF) every 6 hour. Then the mixture was initially purged with nitrogen for 60 min without any irradiation and subsequently monitored under irradiation using GPC (THF) every 6 hour. Following the irradiation period in the presence of nitrogen, the vial was filled with air for 60 min. The mixture was returned to the light reactor and the polymerization was monitored by GPC (THF) every 6 hour again.

7. Reactive Oxygen Species(ROS) measurements

Single oxygen ($^1O_2$) measurements. A 1 mL reaction solvent (DMAc) charged with 0.5 mg/mL **PCs** ($^1O_2$ generator) and 2mM 9,10-dimethylanthracene ($^1O_2$ trapper), which was added into a glass cuvette (1 mm pathlength) and sealed with a rubber septum. The mixture was irradiated under LED light (13 W m^{-1}, 15 mW cm^{-2}) and the absorbance at $\lambda = 379$ nm was recorded by UV-vis spectrophotometer at the indicated times.

Superoxide anion radical ($O_2^{\bullet-}$) measurements. A 1 mL reaction mixture consisting of 0.5 mg/mL **PCs** ($O_2^{\bullet-}$ generator) and 2 mM nitro blue tetrazolium ($O_2^{\bullet-}$ trapper) in DMAc were added into a glass cuvette (1 mm pathlength) and sealed with a rubber septum. The mixture was irradiated under LED light (13 W m^{-1}, 15 mW cm^{-2}) and the absorbance at $\lambda = 280$ nm was recorded by UV-vis spectrophotometer at the indicated times.

8. ESR Detection.

The ROS generated by COFs have been detected by ESR in the presence of DMPO and TEMP, respectively. Typically,30 μL DMPO or TEMP in 1 mL DMAc was mixed with 0.5 mL of COF/ DMAc suspension (2 mg/2 mL). The formed mixture (300-400 μL) was added into the ESR tube. ESR measurements were carried out during the light irradiation with a 500 W xenon lamp ($\lambda > 420$ nm) under the air conditions.

Table S1 TCPP-DMTA-COP-catalyzed PET-RAFT polymerization using different amount catalyst without TEA under air atmosphere.

No.[a]	[MMA]/[CPADB]	Cat. (mg)	Time (h)	$M_{n,GPC}$ [b] (Da)	$M_{n.th.}$ [c] (Da)	M_w/M_n [b]	Conv.[b] (%)	I [d] (%)
1	200/1	5	12	1800	1200	1.38	4.4	65.7
			18	3000	2500	1.4	10.9	81.7
			24	3700	3600	1.37	16.6	97.7
			30	5300	4700	1.27	22.2	90.0
			36	6200	6600	1.28	31.4	105.8
			42	8600	8900	1.28	43.2	104.1
			48	10000	10500	1.23	51.1	104.6
2	200/1	1	12	1400	400	1.2	0.7	29.4
			18	2700	2200	1.35	9.6	80.9
			24	4000	3800	1.26	17.7	95.2
			30	5700	5700	1.2	27.2	100.3
			36	7600	7200	1.15	34.3	94.5
			42	9300	8400	1.15	40.5	90.0
			48	10500	10200	1.17	49.4	96.8
3	200/1	0.5	18	2100	1300	1.39	5.1	61.6
			24	3200	2900	1.33	12.9	90.3
			30	4800	4100	1.26	19.1	86.2
			36	5800	4800	1.21	22.8	82.9
			42	6400	5800	1.22	27.8	90.7
			48	7500	6200	1.18	29.6	83.1

[a] Reaction was performed at room temperature with red LED irradiation(13 W m^{-1}, 15 mW cm^{-2}). [b] Molecular weight, polydispersity index (M_w/M_n) and conversions were determined by GPC analysis (THF as eluent) calibrated to PMMA standard. [c] $M_{n,th}$. = MW (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]).

[d].I (%) = $M_{n.th.}/M_{n,GPC}$ × 100.

Table S2 TCPP-DMTA-COP-catalyzed PET-RAFT polymerization under different concentration of TEA under air atmosphere.

No.[a]	[MMA]/[CPADB]	Cat. (mg)	Time (h)	$M_{\mathrm{n,GPC}}$ [b] (Da)	$M_{\mathrm{n.th.}}$ [c] (Da)	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [b]	Conv.[b] (%)
1	200/1/5	12	3200	2300	1.35	10.2	72.9
		18	4000	3400	1.39	15.8	86.7
		24	5300	4400	1.26	20.8	83.3
		30	6600	5100	1.18	23.9	77.0
		36	8100	7100	1.24	33.9	86.8
		42	10200	8900	1.18	43.1	87.4
		48	13400	11400	1.18	55.6	85.3
2	200/1/10	6	2000	100	1.34	3.5	47.5
		12	3200	2400	1.36	10.7	75.2
		18	5900	4800	1.33	22.8	81.8
		24	8700	6800	1.29	32.8	78.9
		30	11500	9200	1.28	44.5	80.1
		36	16800	11900	1.15	58.1	70.6
		42	20200	14300	1.11	70.1	70.7
3	200/1/20	6	2300	1400	1.43	5.6	60.3
		12	4200	4000	1.38	18.8	95.1
		18	6900	6200	1.24	29.5	90.1
		24	9700	8400	1.16	40.5	86.1
		30	11100	9500	1.16	59.0	108.9
		36	13200	11000	1.14	74.3	114.3
		42	14400	13100	1.18	85.6	121.0

[a] Reaction was performed at room temperature with red LED irradiation(13 W m^{-1}, 15 mW cm^{-2}). [b] Molecular weight, polydispersity index ($M_{\mathrm{w}}/M_{\mathrm{n}}$) and conversions were determined by GPC analysis (THF as eluent) calibrated to PMMA standard. [c] $M_{\mathrm{n,th}}$. = MW (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]). [d.] I (%) = $M_{\mathrm{n.th.}}/M_{\mathrm{n,GPC}} \times 100$.

Table S3 TCPP-DMTA-COP-catalyzed PET-RAFT polymerization under different concentration of TEA under nitrogen atmosphere.

No.[a]	[MMA]/[CPADB]	Cat. (mg)	Time (h)	$M_{n,GPC}$ [b] (Da)	$M_{n.th.}$ [c] (Da)	M_w/M_n [b]	Conv.[b] (%)
1	200/1/0	48	-	-	-	-	-
2	200/1/10	6	1500	600	1.38	1.8	43.9
		12	1800	1200	1.39	4.4	63.0
		18	2100	1300	1.39	5.9	70.7
		24	2000	1500	1.38	5.9	71.1
		30	2100	1200	1.35	4.8	57.9
		36	2200	1200	1.35	4.8	55.7
		42	2400	1100	1.26	4.2	46.5
		48	2200	1200	1.33	4.7	55.2

[a] Reaction was performed at room temperature with red LED irradiation(13 W m^{-1}, 15 mW cm^{-2}). [b] Molecular weight, polydispersity index (M_w/M_n) and conversions were determined by GPC analysis (THF as eluent) calibrated to PMMA standard. [c] $M_{n,th}$. = MW (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]). [d] I (%) = $M_{n.th.}/M_{n,GPC}$ × 100.

Table S4 TCPP-DMTA-COP-catalyzed PET-RAFT polymerization using different monomer.

No.[a]	monomer	Solvent	Gas	Time (h)	Cat. (mg)	$M_{n,GPC}$ [b] (Da)	$M_{n.th.}$ [c] (Da)	M_w/M_n [b]	Conv.[d] (%)
1	DEAEMA	DMAc	air	52	1	13100	12600	1.27	61.7
2	MEMA	DMAc	air	33	1	16500	14400	1.15	70.5
3	BzMA	DMAc	air	18	1	3300	2320	1.34	10.2
4	HPMA	DMAc	air	48	1	11100	11600	1.15	56.5

[a] Reaction was performed at room temperature with red LED irradiation(13 W m^{-1}, 15 mW cm^{-2}) using a ratio of [monomer]:[CPADB]:[TEA]=200:1:10 in 4mL glass vial. [b] Molecular weight, polydispersity index (M_w/M_n) and conversions were determined by GPC analysis (THF as eluent) calibrated to PMMA standard. [c] $M_{n,th}$. = MW (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]). [d].Monomer conversion was determined by ^1H NMR.

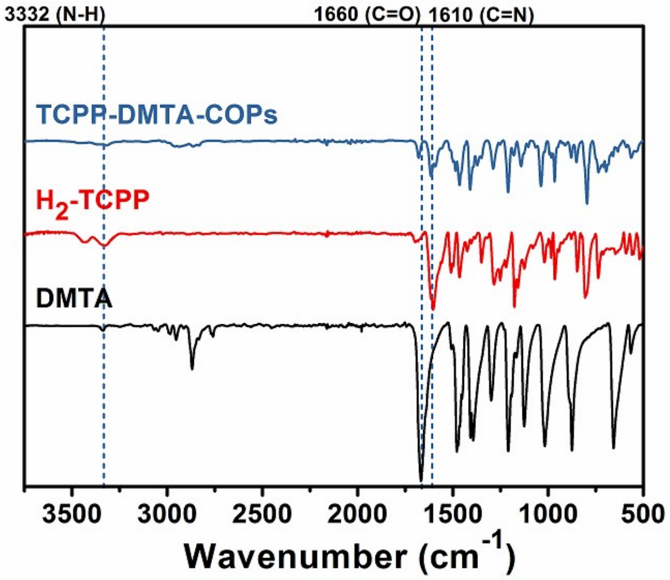


Figure S1. FT-IR spectra of starting materials and **TCPP-DMTA-COP.**

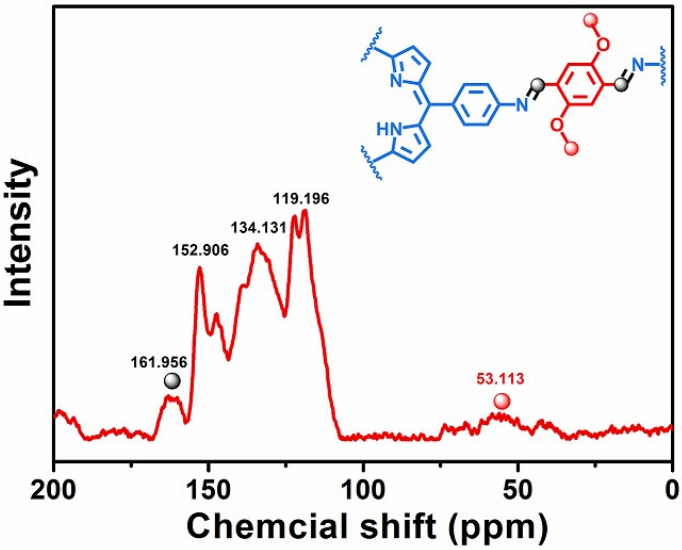


Figure S2. ^{13}C CP-MAS solid-state NMR spectra of **TCPP-DMTA-COP.**

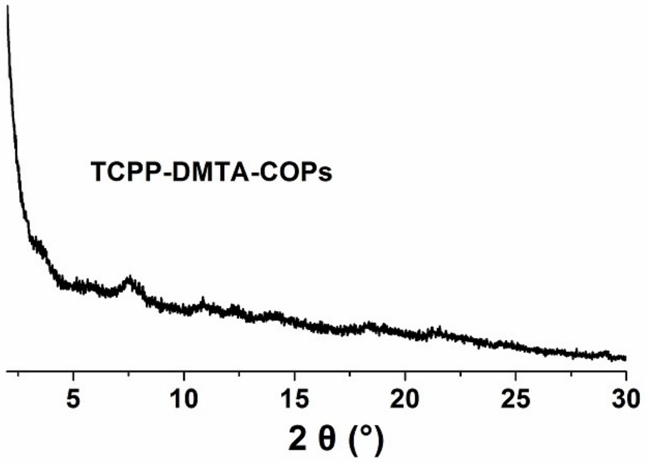


Figure S3. P-XRD pattern of **TCPP-DMTA-COP.**

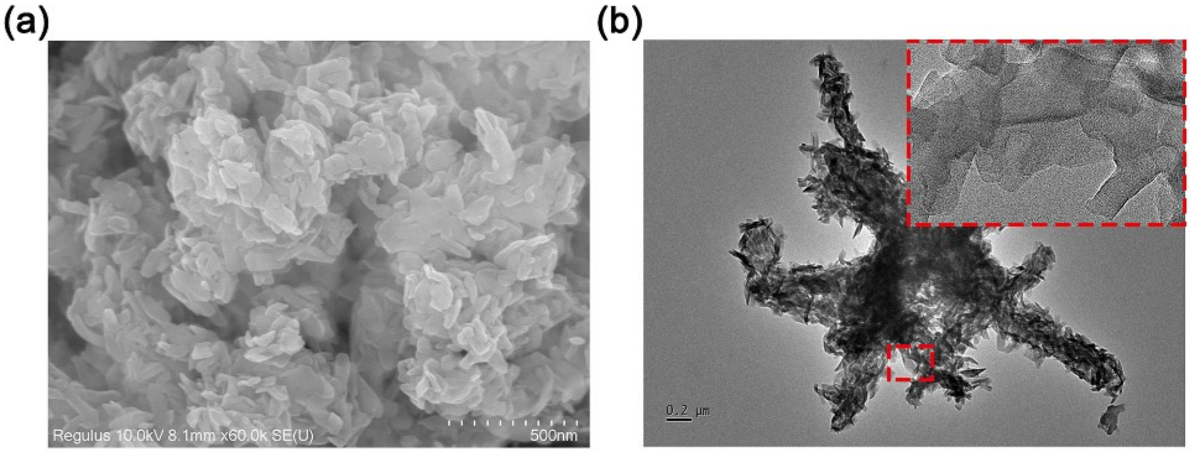


Figure S4. (a) SEM images and (b) TEM images of **TCPP-DMTA-COP.**

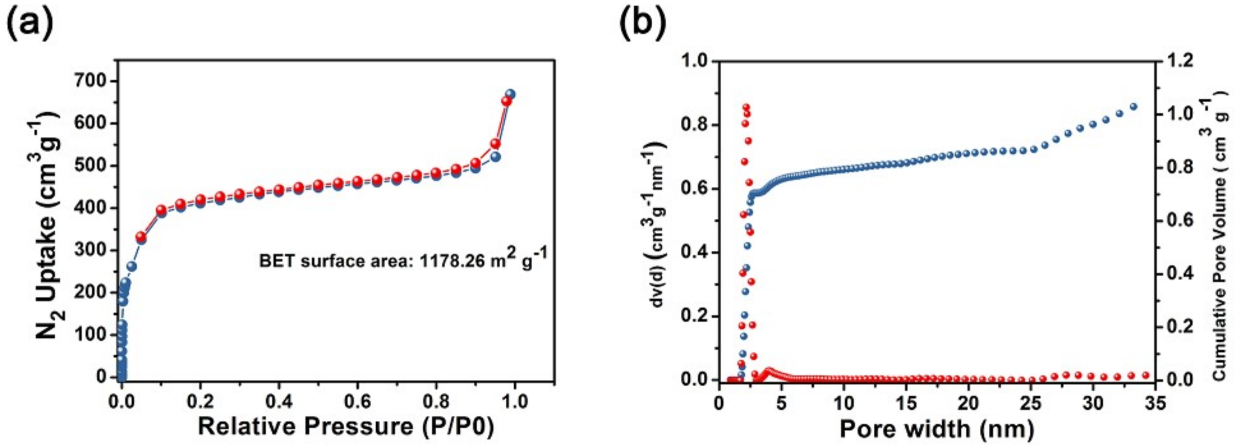


Figure S5. (a) N_2 adsorption-desorption isothermal (blue represents the adsorption process, red represents the process of desorption) and (b) pore-width distribution (red line) and pore volume (blue line) of **TCPP-DMTA-COP.**

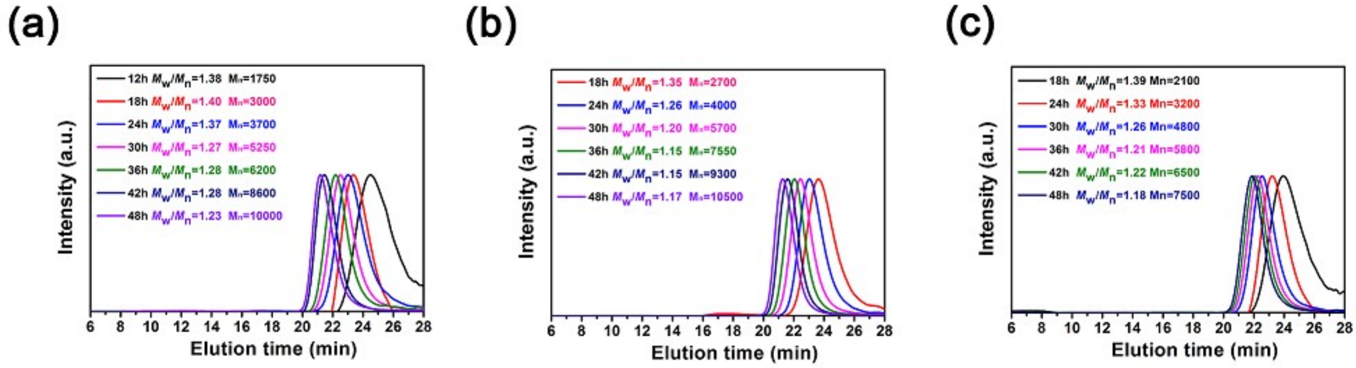


Figure S6. TCPP-DMTA-COP mediated polymerization of MMA in DMAc with a reaction stoichiometry of [MMA]:[CPADB]=200:1 under red LED light irradiation (13 W m^{-1}, 15 mW cm^{-2}) in air condition. (a), (b), (c)GPC trace of different dosage of **TCPP-DMTA-COP** ($m_{\mathbf{cat.}}$= 5 mg, 1 mg, 0.5 mg).

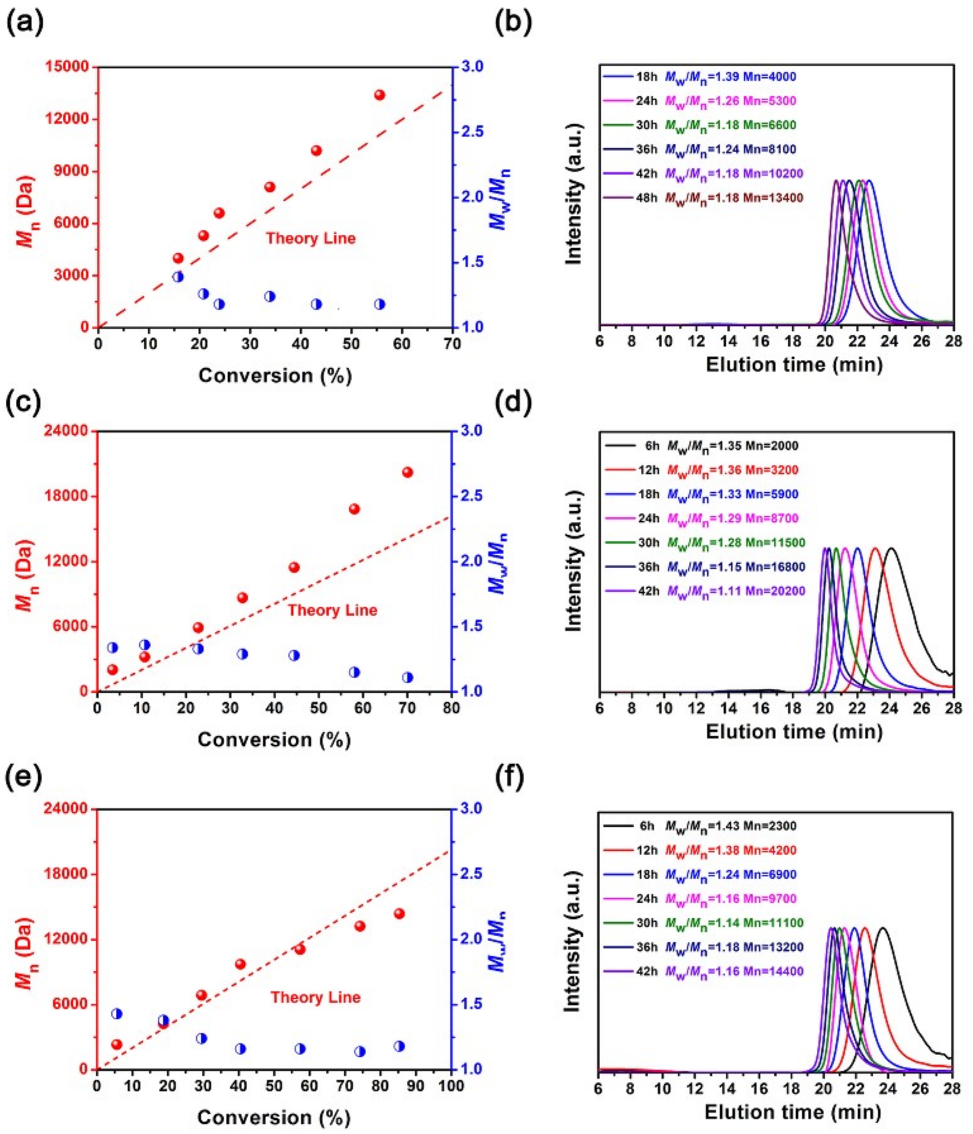


Figure S7. TCPP-DMTA-COP (1 mg) mediated polymerization of MMA in DMAc with a reaction stoichiometry of [MMA]:[CPADB]=200:1 under red LED light irradiation (13 W m^{-1}, 15 mW cm^{-2}). (a), (b) Evolution of M_n and M_w/M_n with the increasing monomer conversion and kinetic plots of ln(M_0/M_t) *vs.* exposure time with TEA ([CPADB]:[TEA]=1:5) in aerobic condition. (c), (d) Evolution of M_n and M_w/M_n with the increasing monomer conversion and kinetic plots of ln(M_0/M_t) *vs.* exposure time with TEA ([CPADB]:[TEA]=1:10) in aerobic condition. (e), (f) Evolution of M_n and M_w/M_n with the increasing monomer conversion and kinetic plots of ln(M_0/M_t) *vs.* exposure time with TEA ([CPADB]:[TEA]=1:20) in aerobic condition.

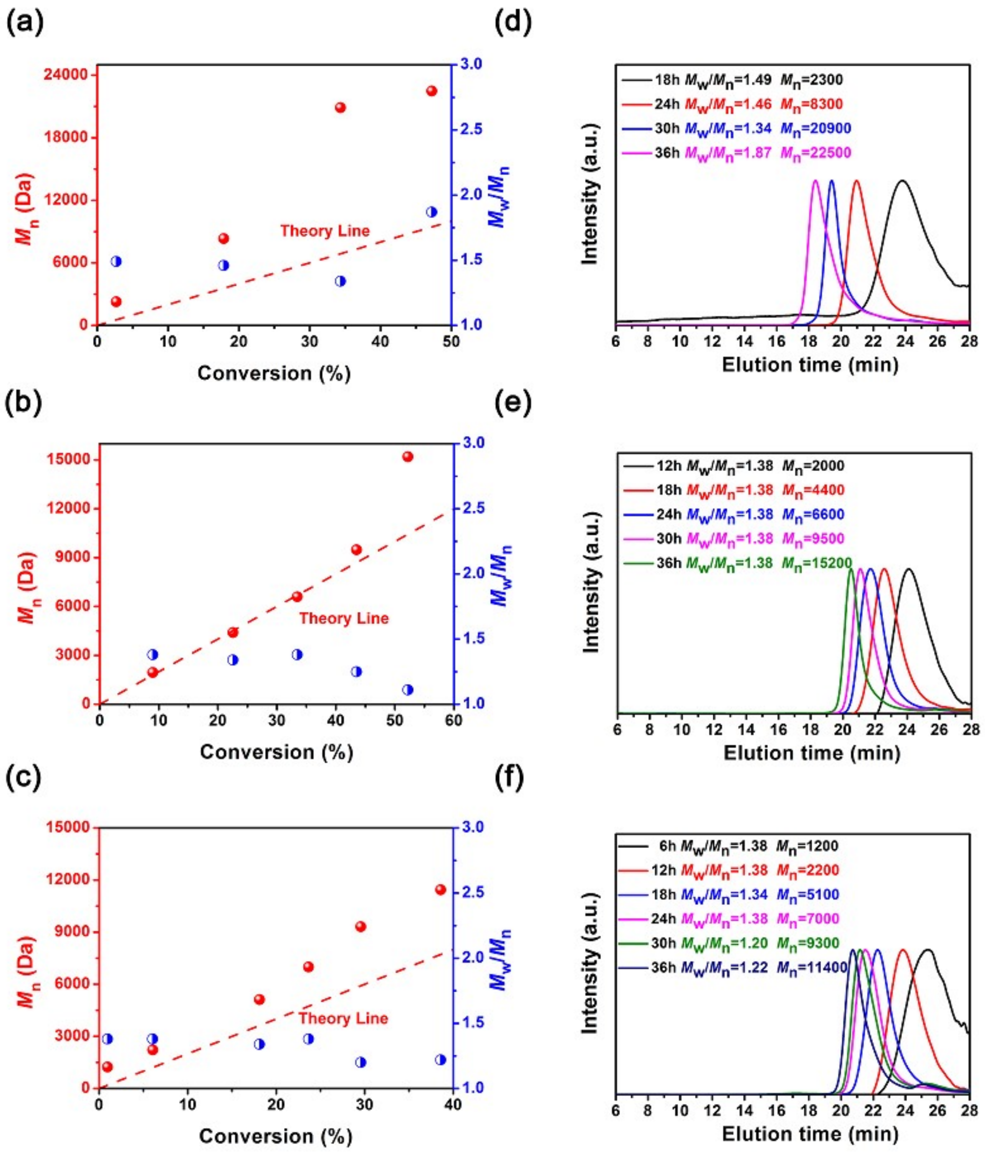


Figure S8. The influence of glass vial volume on polymerization processes, using **TCPP** ($m_{\mathbf{cat.}}$ = 1 mg) as PCs under the red LED light irradiation (13 W m^{-1}, 15 mW cm^{-2}), assisting with TEA ([CPADB]:[TEA] = 1 : 10) in air condition (a), (b) 20 mL of glass volume, (c), (d) 12 mL of glass volume, (e), (f) 4 mL of glass volume.

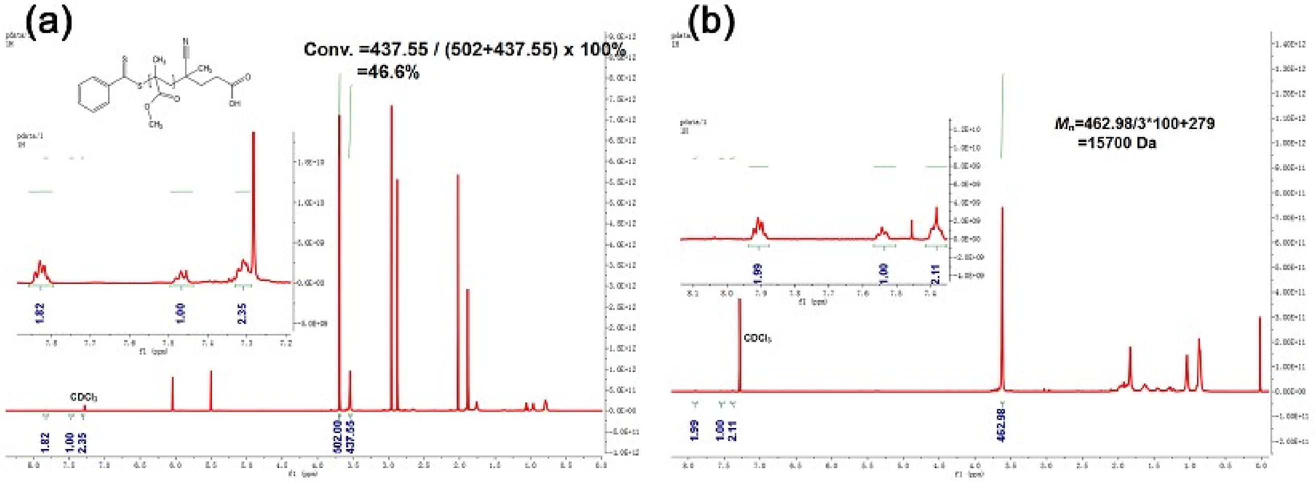


Figure S9. ^{1}H NMR spectra of (a) obtained crude product in $CDCl_3$ and (b) re-precipitation polymer in $CDCl_3$ ([MMA] : [CPADB] : [TEA]= 200 : 1 : 10, **TCPP-DMTA-COP** 1 mg in aerobic condition).

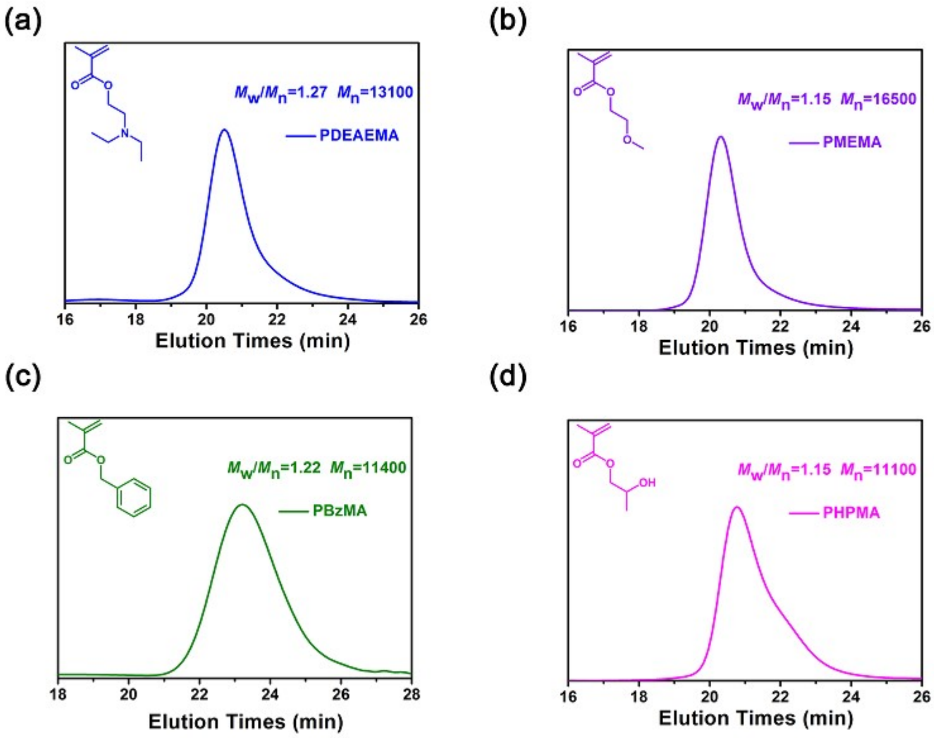


Figure S10. GPC traces for different monomers.

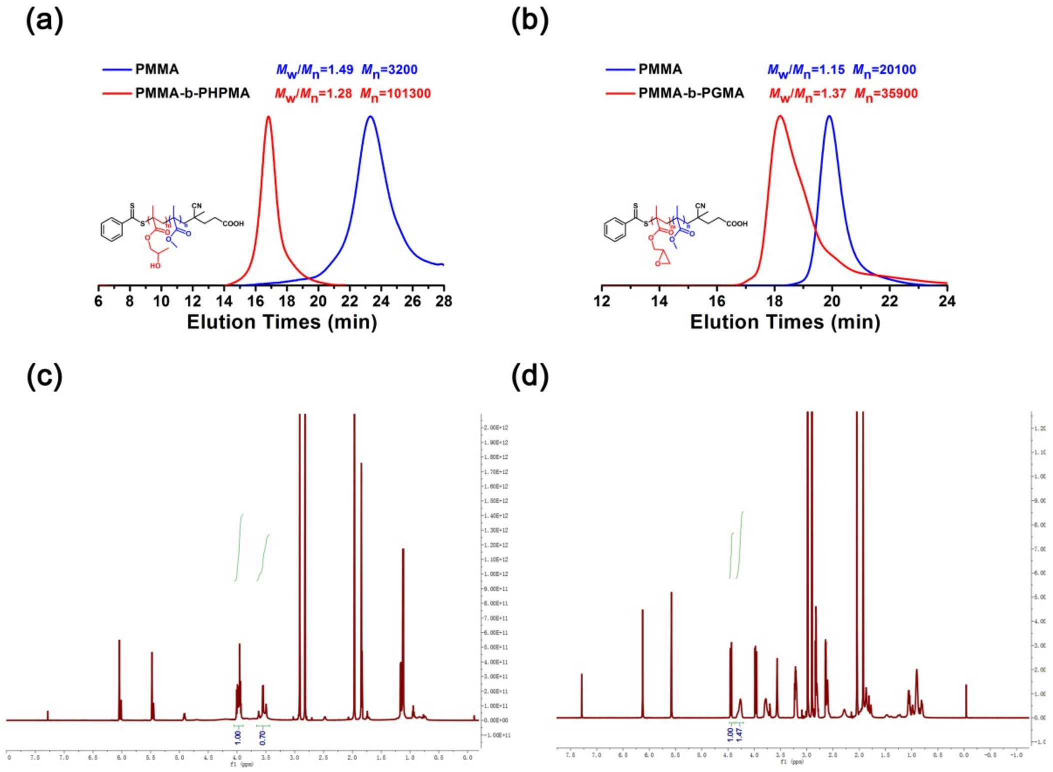


Figure S11.(a) (b) GPC traces of micro-initiators and **block copolymers**. (c) (d)^{1}H NMR spectra of **block copolymers** in $CDCl_3$.

Table S5. The chain extension reaction results of **TCPP-DMTA-COP**-catalyzed PET-RAFT polymerization under aerobic condition.

No.[a]	monomer	DP	Time (h)	Cat. (mg)	$M_{n,GPC}$ [b] (Da)	$M_{n.th.}$ [c] (Da)	M_w/M_n [b]	Conv.[d] (%)
1	HPMA[e]	1000	48	1	101300	87900	1.28	58.8
3	GMA[f]	500	48	1	35900	62300	1.37	59.5

[a] Reaction was performed at room temperature with red LED irradiation(13 W m^{-1}, 15 mW cm^{-2}). [b] Molecular weight, polydispersity index (M_w/M_n) and conversions were determined by GPC analysis (THF as eluent) calibrated to PMMA standard. [c] $M_{n,th.}$ = MW (initiator) + MW (monomer) × Conv. × ([monomer]/[initiator]). [d]. Monomer conversion was determined by ^{1}H NMR. [e] The macro-CTA (M_n = 3200 g/mol, M_w/M_n=1.49) of **PMMA-*b*-PHPMA** chain extension reaction was used. [f] The macro-CTA (M_n = 20100 g/mol, M_w/M_n=1.15) of **PMMA-*b*-PGMA** chain extension reaction was used.

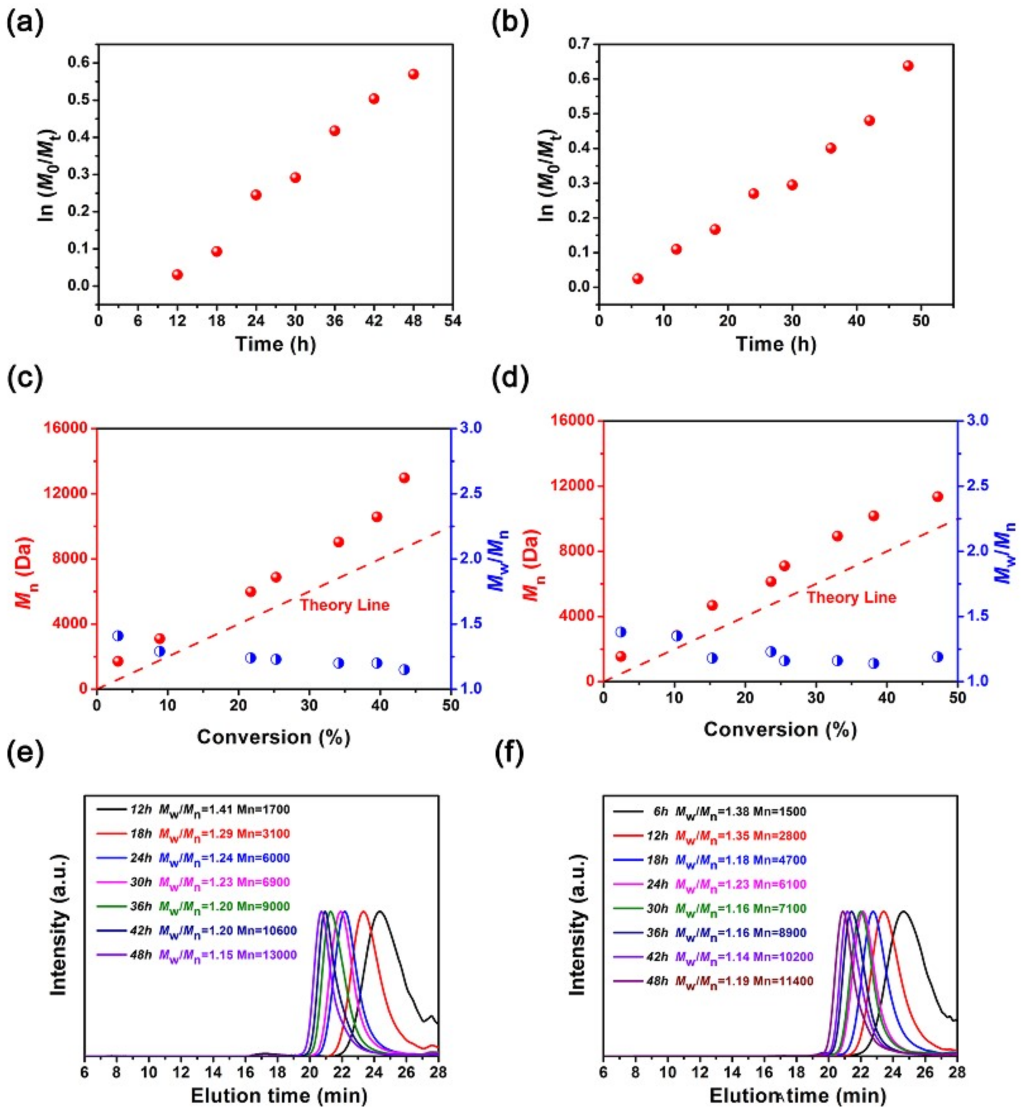


Figure S12. **TCPP-DMTA-COP** (1 mg) mediated polymerization of MMA in DMAc with a reaction stoichiometry of [MMA]:[CPADB] = 200 : 1 under red LED light irradiation (13 W m^{-1}, 15 mW cm^{-2}) in 4 mL glass vial with different amine. (a), (b), (c) TEOA ([CPADB]:[TEOA]=1:10), (d), (e), (f) PMDETA ([CPADB]:[PMDETA]=1:10).

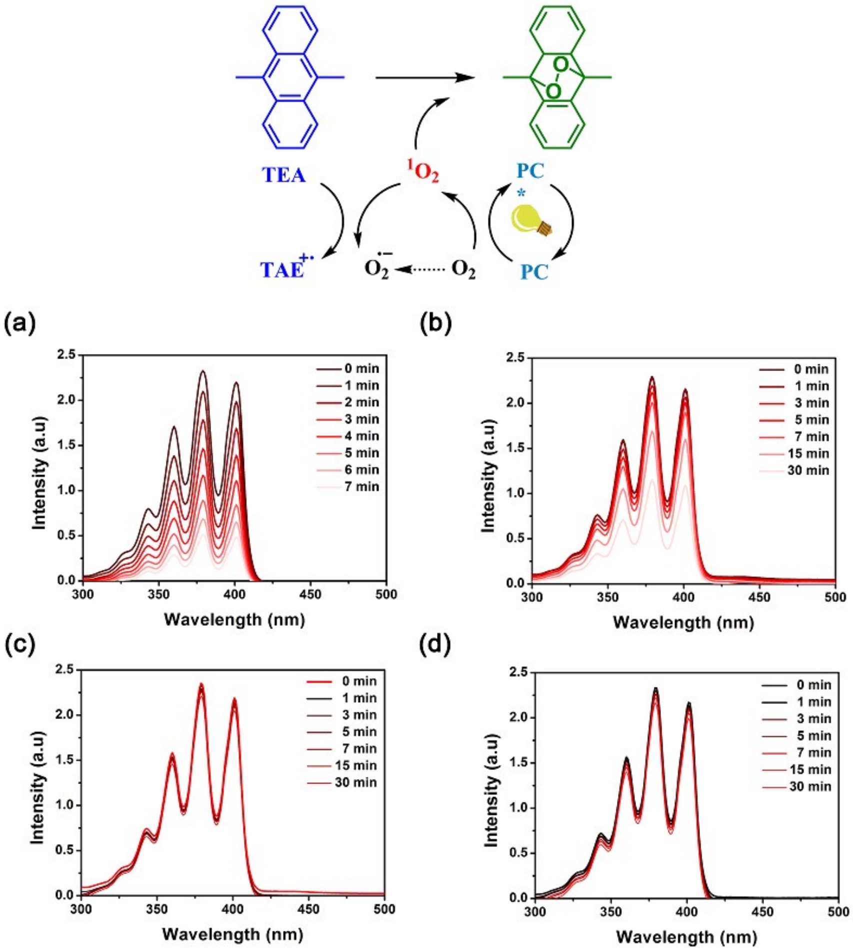


Figure S13. UV-vis spectra of the 9,10-dimethylanthracene solution with a serious of TEA concentration (1 eq = 13.4 μL) in aerobic condition under red light irradiation, (a) 0 eqv. TEA, (b) 0.5 eqv. TEA, (c) 5 eqv. TEA, (d). 10 eqv. TEA.

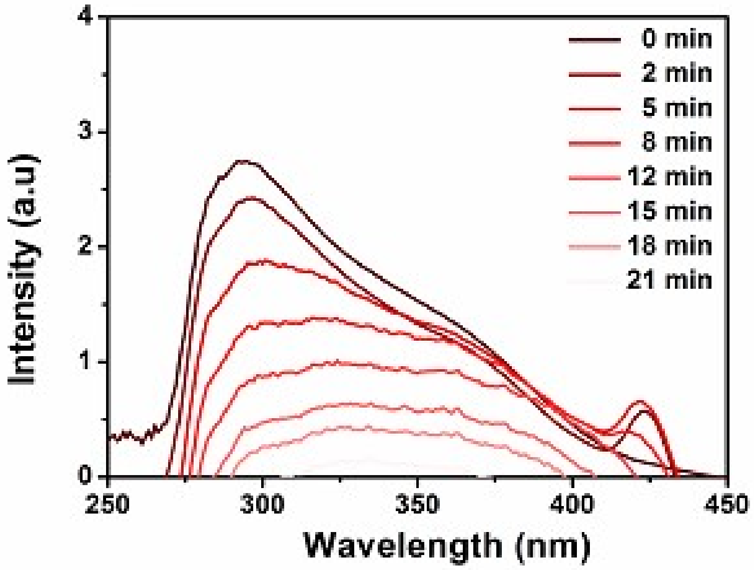


Figure S14. UV-vis spectra of the NBT solution with **TCPP-DMTA-COP** in aerobic condition under red light irradiation.

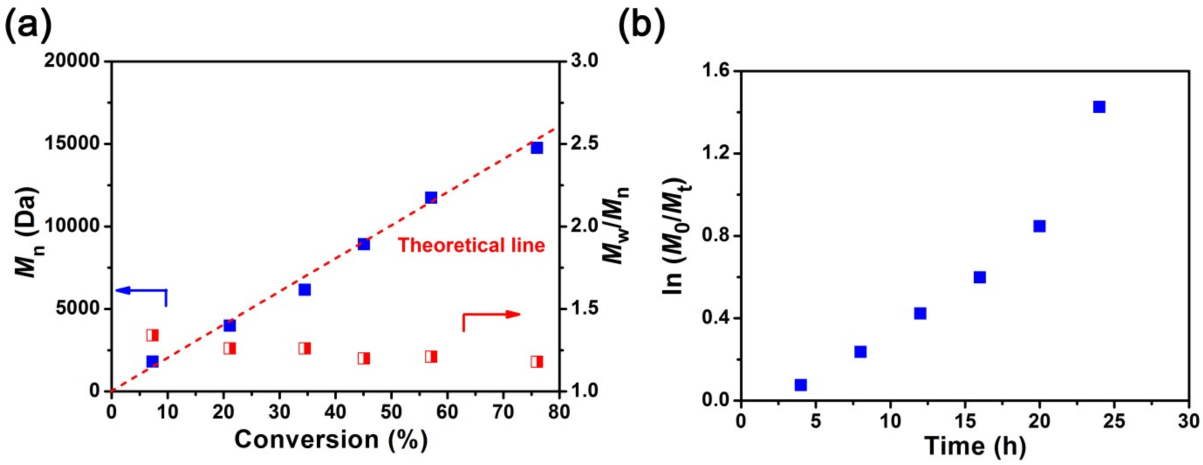


Figure S15. TCPP-DMTA-COP (m = 1mg) was used as catalyst for oxygen-containing polymerization under white light induction ([MMA]:[CPADB]:[TEA] = 200:1:10). (a) the relationship between molecular weight, molecular weight distribution and conversion, and (b) the effect of polymerization kinetics

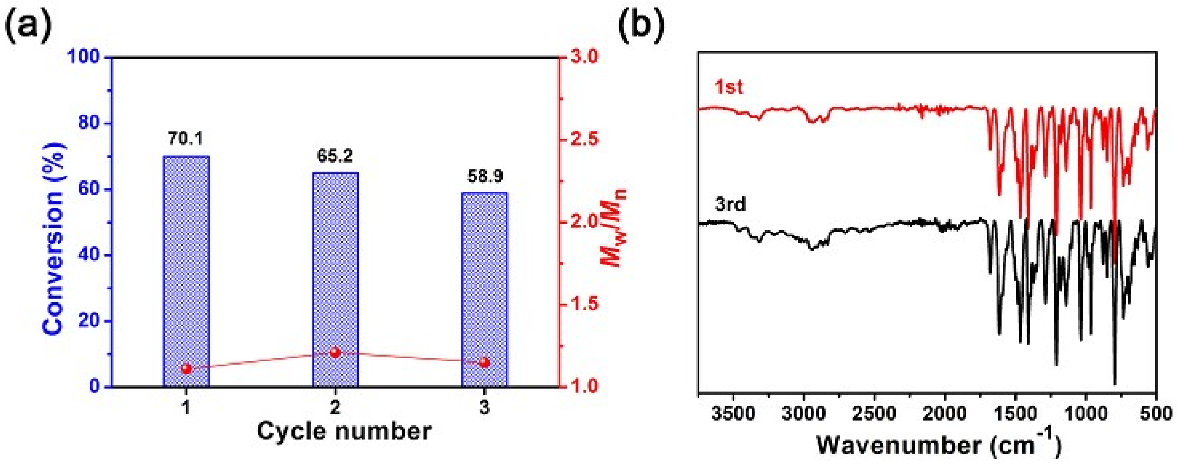


Figure S16. TCPP-DMTA-COP catalytic cycle experiment. (a) Monomer conversion and molecular weight distribution of polymers obtained from three cycles and (b) FT-IR characterization of catalysts before and after catalysis.

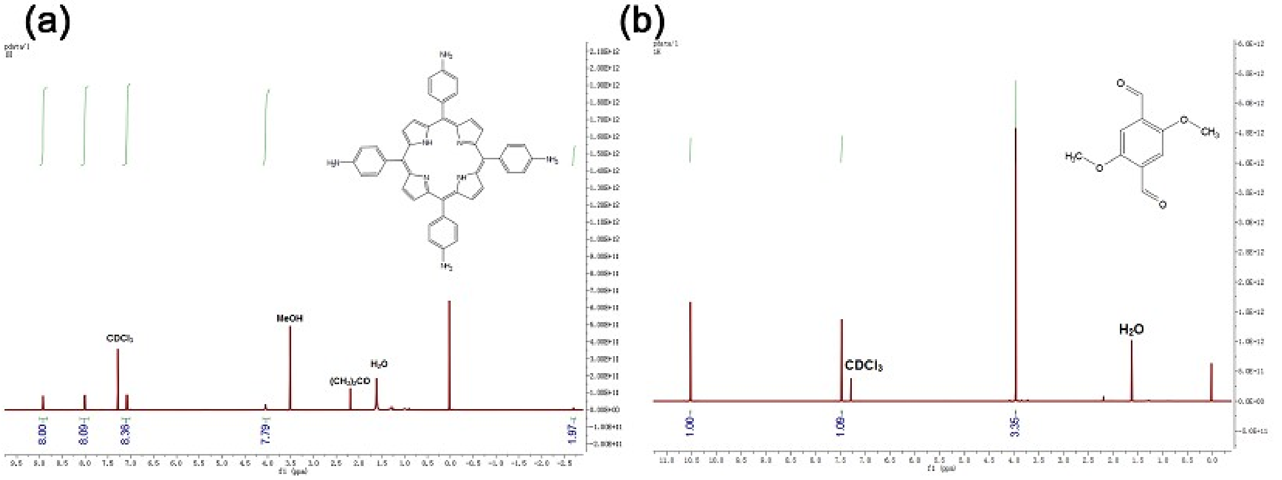


Figure S17. ^{1}H NMR spectra of (a) TCPP in $CDCl_3$ and (b) ^{1}H NMR spectra of DMTA in $CDCl_3$.