Electronic Supplementary Information

Organo-Photocatalysts for Photoinduced Electron Transfer – Reversible Addition-Fragmentation Chain Transfer (PET-RAFT) Polymerization

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Photopolymerization setup

Photopolymerization was carried out in the reaction vessel where the reaction mixtures are irradiated by RS Component PACK LAMP RGB blue/green/red LED lights (4.8 W, λ_{max} = 435 nm (blue), 530 nm (green) and 635 nm (red)) showed below. The distance of the samples to light bulb was 6 cm. The RGB multi-colored LED light bulb with remote control was purchased from RS Components Australia.

Additional data:

Semi-quantitative calculation of oxygen amount in the reaction vessel:

1) 0.9 mL FTNIR cell: 0.7 mL reaction solution and 0.2 mL free air space;

2) Dissolved oxygen amount in 0.7 mL reaction solution: Dissolved oxygen concentration in acrylic monomer were reported to be in the 0.6~2 mM range.[5] Dissolved oxygen concentration in DMSO was reported to be 0.33 mM.[6] While taking the highest concentration into calculation and reaction solution roughly consisting of 0.35 mL of MMA and 0.35 mL of DMSO, the total dissolved oxygen amount in reaction solution was estimated to be:

$$2\ \text{mM} \times 0.35\ \text{mL} + 0.33\ \text{mM} \times 0.35\ \text{mL} = 8.19 \times 10^{-4}\ \text{mmol};$$

3) Oxygen amount in 0.2 mL free air space: The oxygen density in normal temperature (20 ^{o}C) and pressure (1 atm) is 1.331 g/L. The volume ratio of oxygen in air is roughly 20%. The total oxygen amount in free space was estimated to be:

$(0.2\ \text{mL} \times 20\% \times 1.331\ \text{g/L}) / 32$ (molecular weight of oxygen) $= 1.66 \times 10^{-3}$ mmol;

4) The total oxygen in reaction vessel is 2.48×10^{-3} mmol;

5) TEA amount in 0.7 mL reaction solution with the molar ratio of [MMA]:[CPADB]:[EY]:[TEA] = 200 : 1 : 0.02 : 0.1 is 1.65×10^{-3} mmol;

6) TEA amount in 0.7 mL reaction solution with the molar ratio of [MMA]:[CPADB]:[EY]:[TEA] = 200 : 1 : 0.02 : 1 is 16.5×10^{-3} mmol.

Therefore, it is concluded that while assuming one TEA molecule transfers one electron to molecular oxygen, the TEA amount in (5) is not enough to reduce all oxygen in the reaction vessel.

Table S1. PET-RAFT polymerization of MMA with different TEA concentrations in the absence of oxygen

TEA concentration ([CPADB]/[TEA])	8 h			12 h		
	Conv. (%)	Mn	PDI	Conv. (%)	Mn	PDI
1/0	31.8	7 520	1.20	52.1	10 400	1.14
1/0.02	38.7	9 250	1.19	49.8	12 080	1.14
1/0.1	36.7	9 880	1.21	50.7	12 490	1.13
1/1	28.1	7 800	1.18	66.9	15 800	1.20

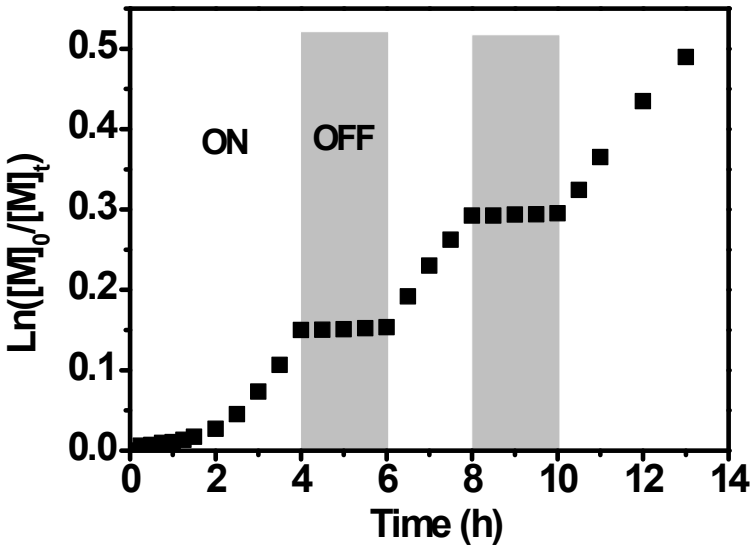

Figure S1. "ON/OFF" study for PET-RAFT polymerization of MMA mediated by eosin Y in the absence of oxygen.

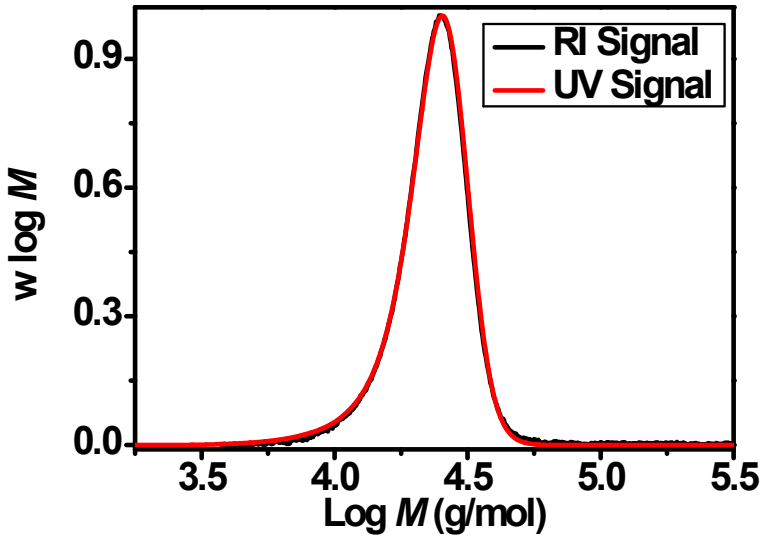

Figure S2. Molecular weight distribution of RI (black line) and UV (red line) signal for purified PMMA prepared by PET-RAFT polymerization mediated by EY/TEA in the presence of oxygen, detected by dual RI and UV detector. $M_{n,GPC}$ = 21 710 g/mol, M_w/M_n = 1.12.

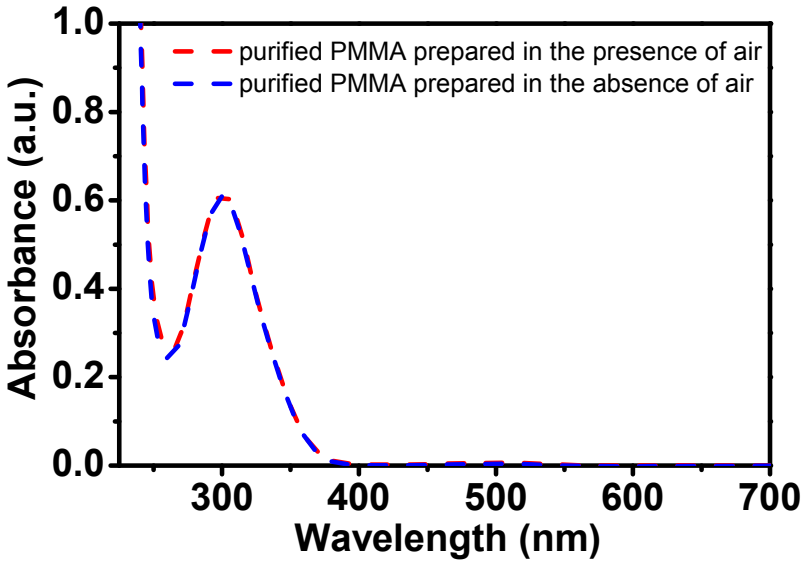

Figure S3. UV-vis spectrum for purified PMMA prepared by PET-RAFT technique mediated by EY/TEA in the presence of oxygen ($M_{n,\,GPC}$ = 21 710 g/mol, M_w/M_n = 1.12) and in the absence of oxygen ($M_{n,\,GPC}$ = 20 550 g/mol, M_w/M_n = 1.12).

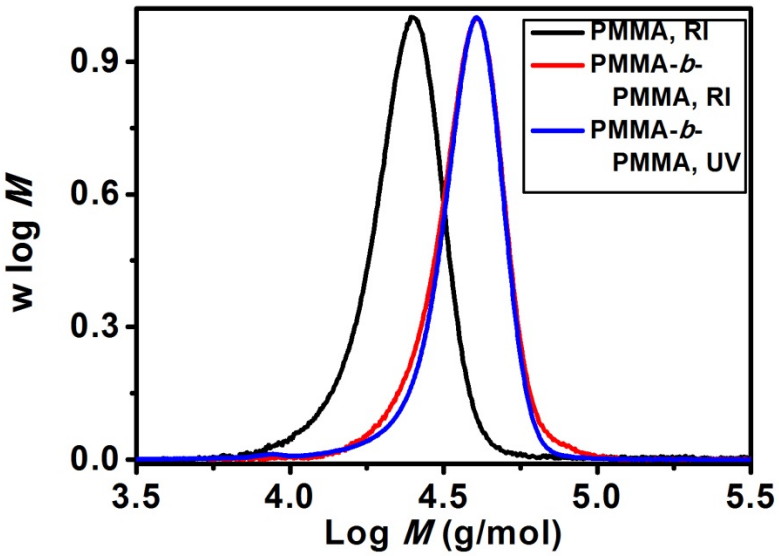

Figure S4. Molecular weight distributions for PMMA (RI signal) and its chain extension diblock copolymer PMMA-*b*-PMMA (RI and UV signal) prepared by PET-RAFT technique. PMMA: $M_{n,\ GPC}$ = 21 710 g/mol, M_w/M_n = 1.12; PMMA-*b*-PMMA: $M_{n,\ GPC}$ = 33 200 g/mol, M_w/M_n = 1.13.

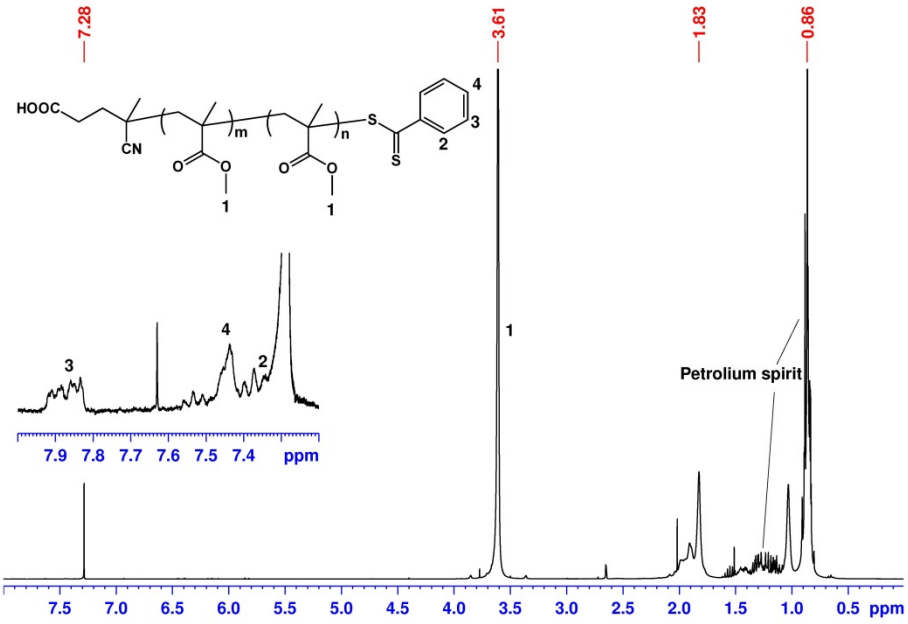

Figure S5. ^{1}H NMR spectrum ($CDCl_3$) for purified diblock copolymer PMMA-*b*-PMMA prepared by PET-RAFT polymerization mediated by EY/TEA in the absence of oxygen.

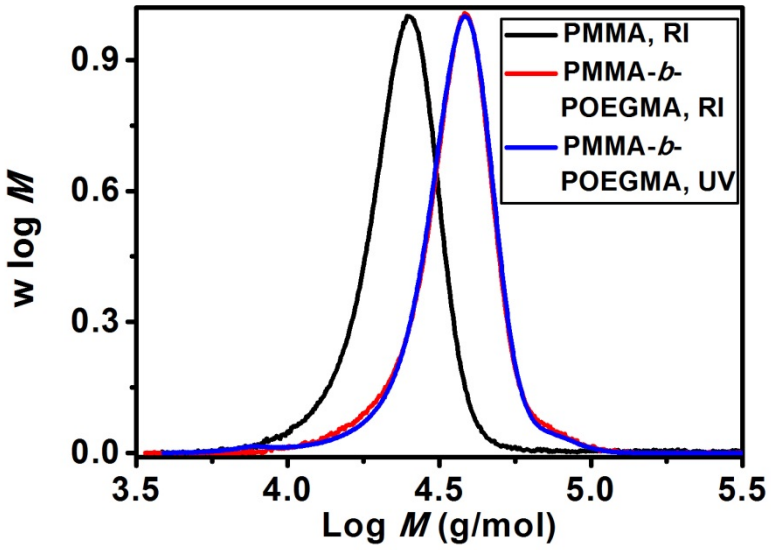

Figure S6. Molecular weight distributions for PMMA (RI signal) and its chain extension diblock copolymer PMMA-*b*-POEGMA (RI and UV signal) prepared by PET-RAFT technique. PMMA: $M_{n,\,GPC}$ = 21 710 g/mol, M_w/M_n = 1.12; PMMA-*b*-POEGMA: $M_{n,\,GPC}$ = 32 700 g/mol, M_w/M_n = 1.14.

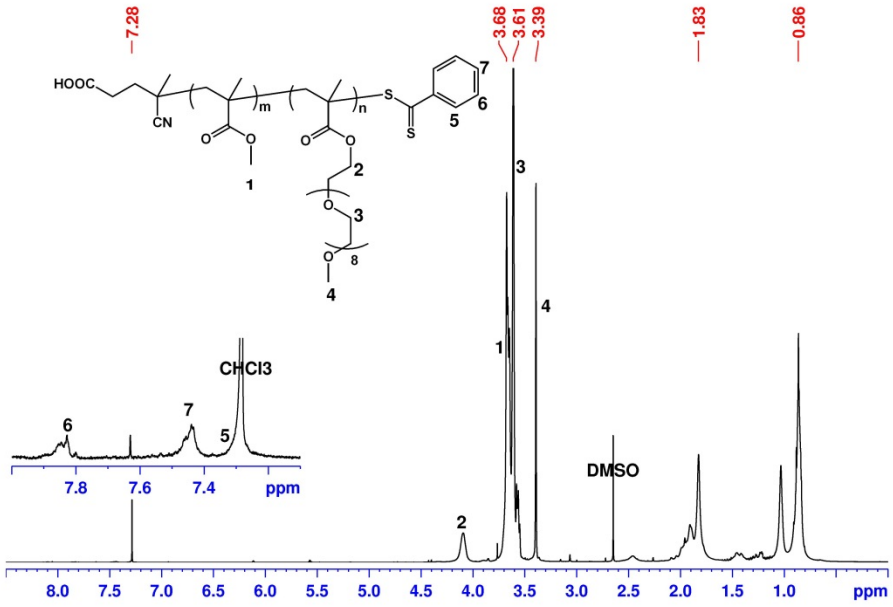

Figure S7. ^{1}H NMR spectrum ($CDCl_3$) for purified diblock copolymer PMMA-*b*-POEGMA prepared by PET-RAFT polymerization mediated by EY/TEA.