Photoinduced Metal-Free Atom Transfer Radical Polymerization of Biomass Based Monomers

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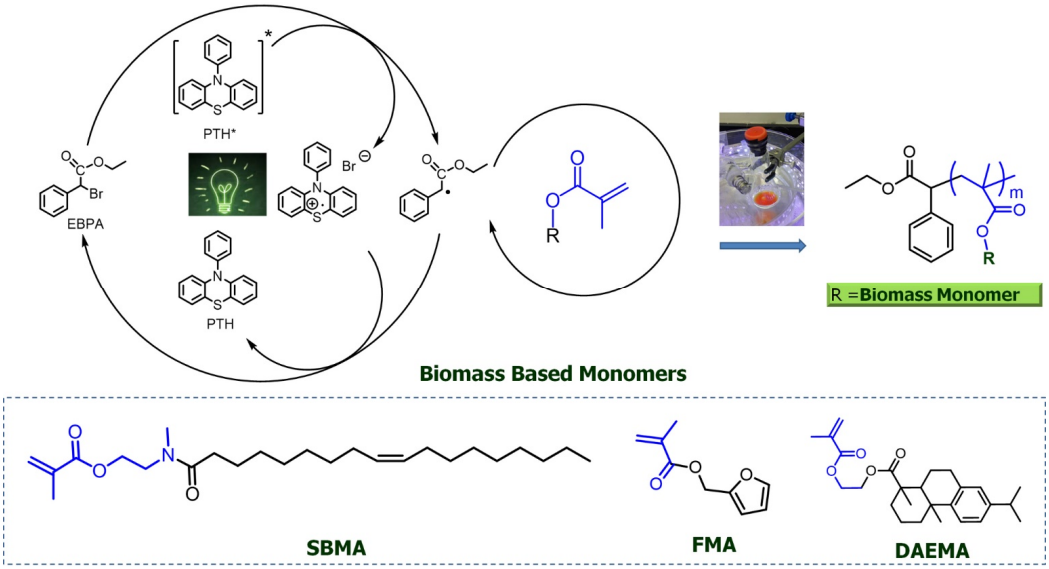
Supporting Information

Scheme S1. Metal-free ATRP of biomass based monomers



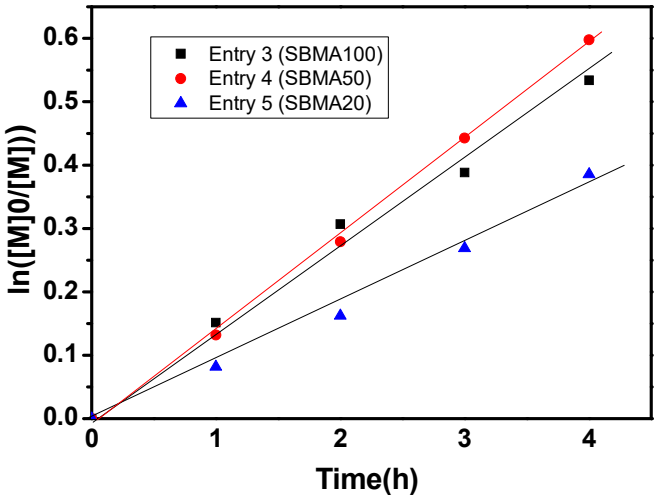


Figure S1. Semilogarithmic kinetic plots of polymerization of SBMA with metal-free ATRP with [SBMA]/[EBPA]:[Catalyst]=100, 50 or 20:1:0.1.

Table S1. Optimization of photoinduced ATRP of FMA[a]

Entry	[FMA]:[EBPA]:[catalyst]	Conv. (%)	M_n in theory[d]	M_n by GPC	Đ
S1[b]	50:0:0	17	N/A	107.1 k	1.64
S2[c]	50:0:0	0	N/A	N/A	N/A
S3	50:0:0	0	N/A	N/A	N/A
S4[c]	50:1:0.1	19	1.9 k	2.3 k	1.21
S5	50:1:0.1	31	3.1 k	2.6 k	1.31
S6	20:1:0.1	25	1. 1 k	2.5 k	1.29

[a] Reaction conditions: FMA (20, 50 or 100 equiv), EBPA (1 equiv), PTH (0.1 equiv), FMA/THF = 1:2 (v/v), 4 h, at room temperature with irradiation by 380 nm UV light (LED strips with 0.05 mW/cm UV light intensity); [b] Irradiation by 2.2 mW/cm UV light; [c] Irradiation by visible light (with 0.07 mW/cm UV light intensity).[d] Calculated based on conversion obtained by ^{1}H NMR.

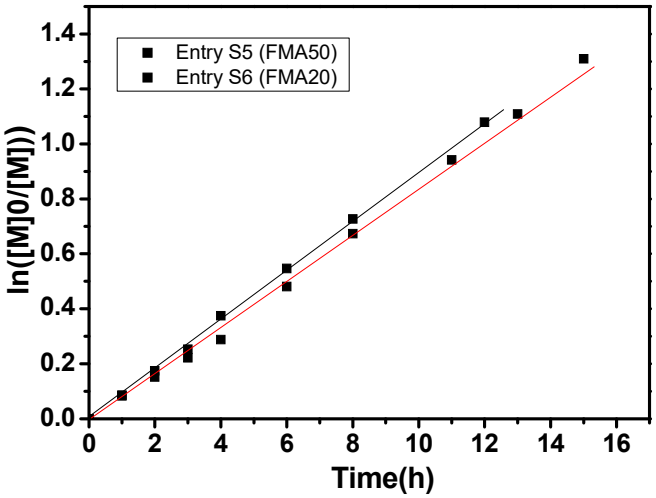
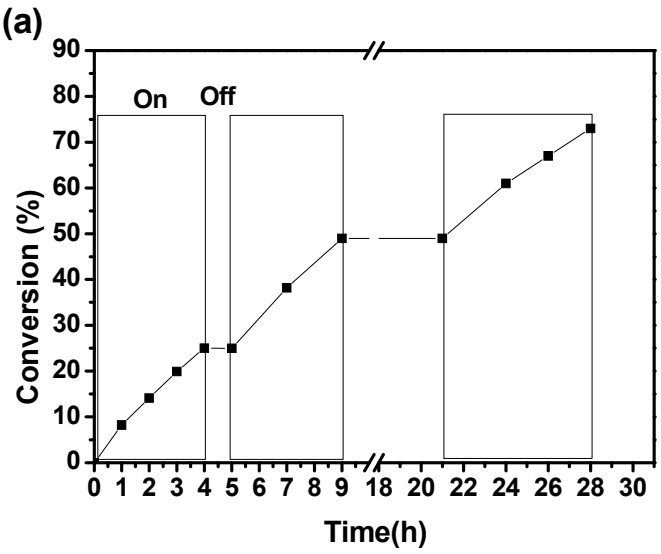


Figure S2. Semilogarithmic kinetic plots of polymerization of FMA with metal-free ATRP under condition [FMA]/[EBPA]= 50 or 20:1.



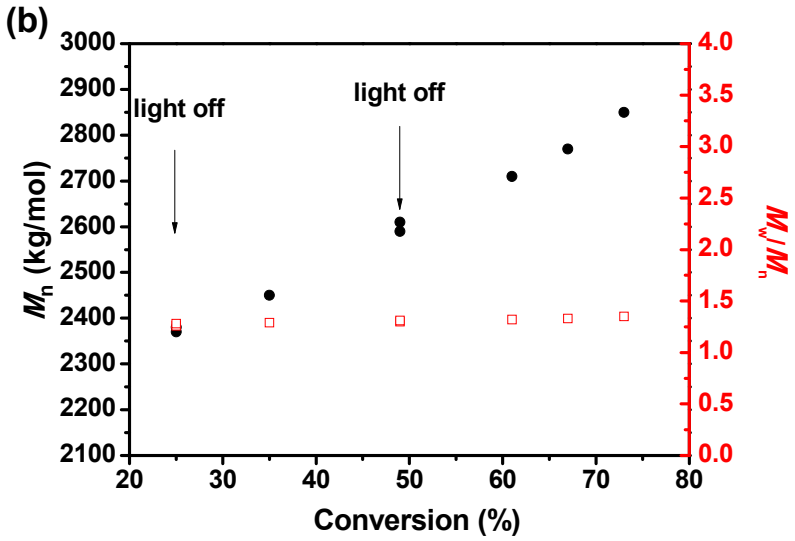


Figure S3. Preparation of PFMA with metal-free ATRP of FMA (Table 2, entry 4) (a) conversion vs time with repeated "on-off"; (b) number-average molecular weight (M_n) and dispersity (M_w/M_n) vs conversion with repeated "on-off".

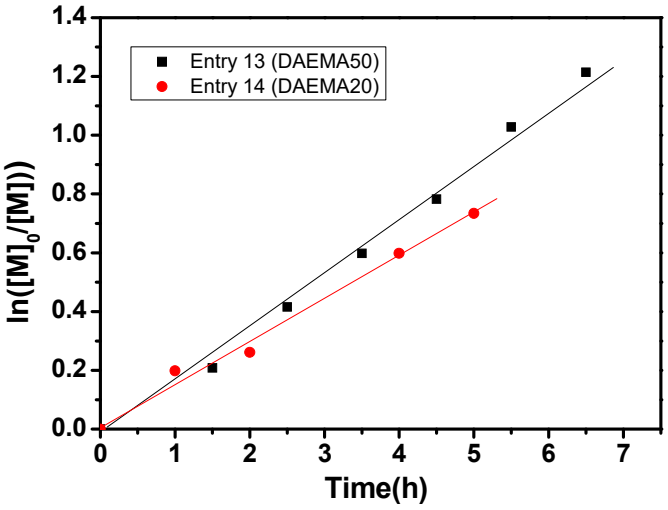


Figure S4. Semilogarithmic kinetic plots of polymerization of DAEMA with metal-free ATRP under condition [DAEMA]:[EBPA]= 50 or 20:1.

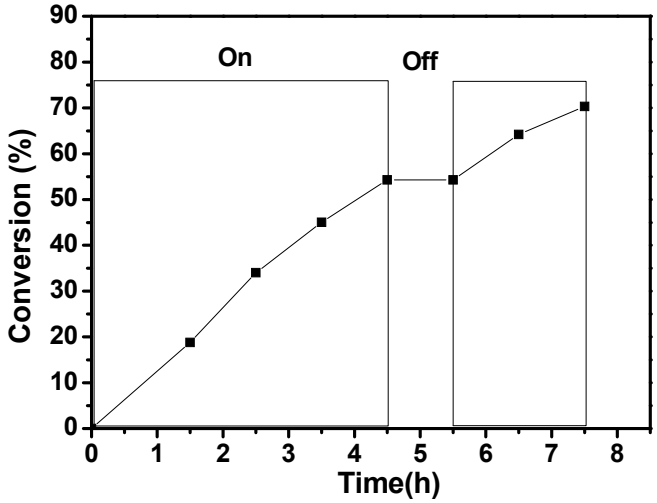
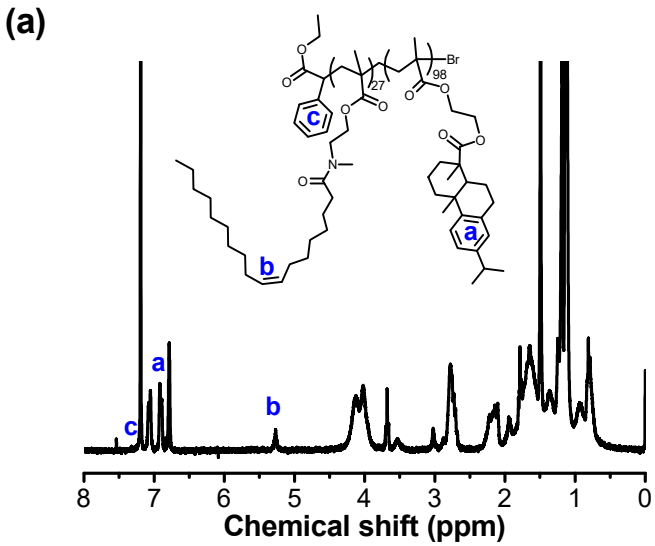


Figure S5. DAEMA conversion vs time with light "on-off" (Table 2, entry 5).



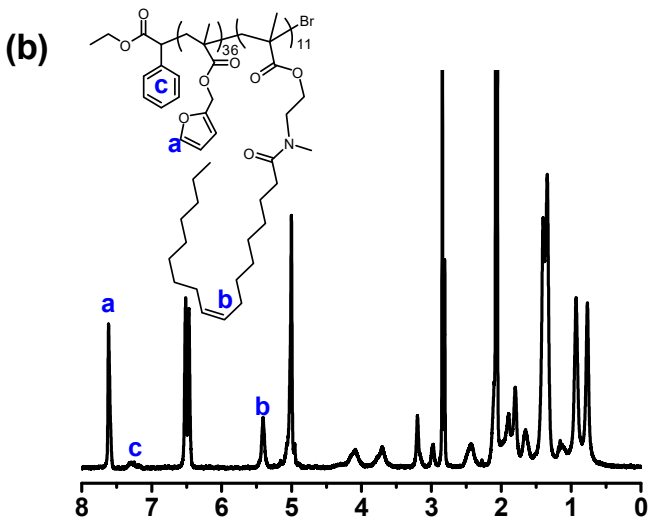
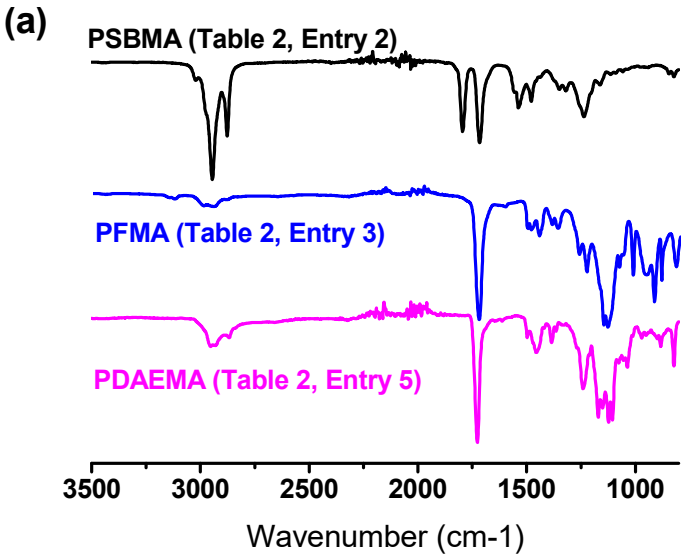


Figure S6. (a) ^{1}H NMR spectra of PSBMA$_{27}$-*b*-DAEMA$_{98}$ (Table 3, entry 2); (b) ^{1}H NMR of PFMA$_{36}$-*b*-PSBMA$_{11}$ (Table 3, entry 3).



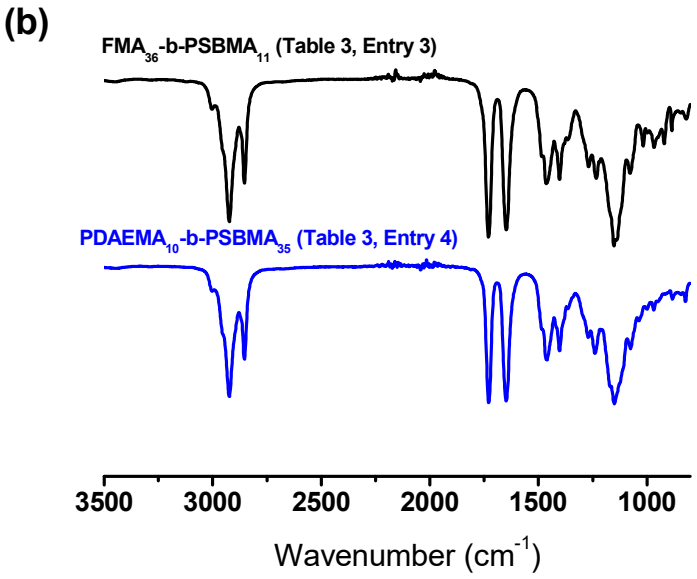


Figure S7. FTIR spectra (a) homopolymers; (b) diblock copolymers.

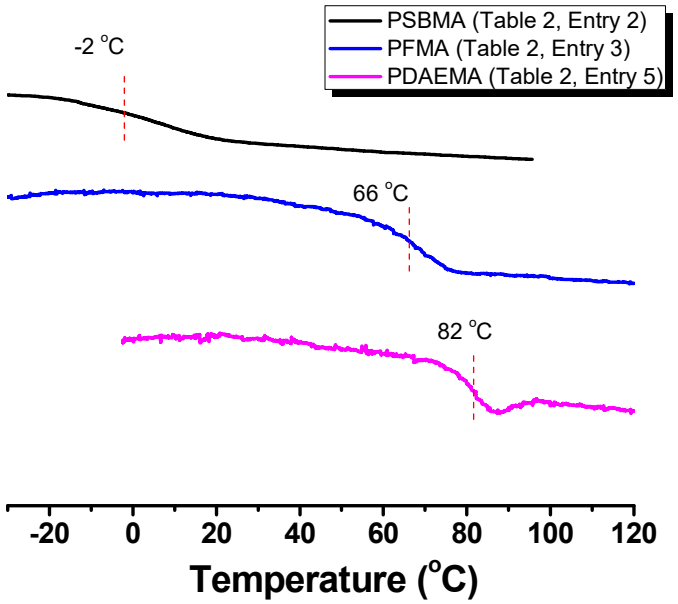


Figure S8. DSC curves of homopolymers.