Electronic Supplementary Material (ESI) for Green Chemistry.

Metal-free ATRP "Grafting From" Technique for Renewable Cellulose Graft Copolymers

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Support Information

Hydrolysis of EC graft copolymer EC-*g*-PLMA$_{250}$

In order to confirm the structure of ethyl cellulose-based graft copolymer and determine their molecular weight and polydispersity index of the grafting side chain polymer, hydrolysis of EC in EC-*g*-PLMA$_{250}$ was carried out. EC-*g*-PLMA$_{250}$ was used representative sample to perform hydrolysis. Typical hydrolysis process was described as[1]: Firstly, 12 mL THF, 6 mL (1mol/mL) sodium hydroxide/methanol solution and 150 mg EC-*g*-PLMA$_{250}$ were charged into a round bottom flask equipped with magnetic stirrer. The mixture was stirred at room temperature for 72 hours to hydrolyze the EC backbone to get the polymer PLMA in the side chain. After hydrolysis, hydrochloric acid (1mol/L) was used to neutralize the solution to neutral. Secondly, PLMA in aqueous solution was extracted by THF. PLMA in THF solution was passed through a filter to remove the solid salt and precipitated in cold methanol three times. Finally, the collected PLMA was dried to constant weight.

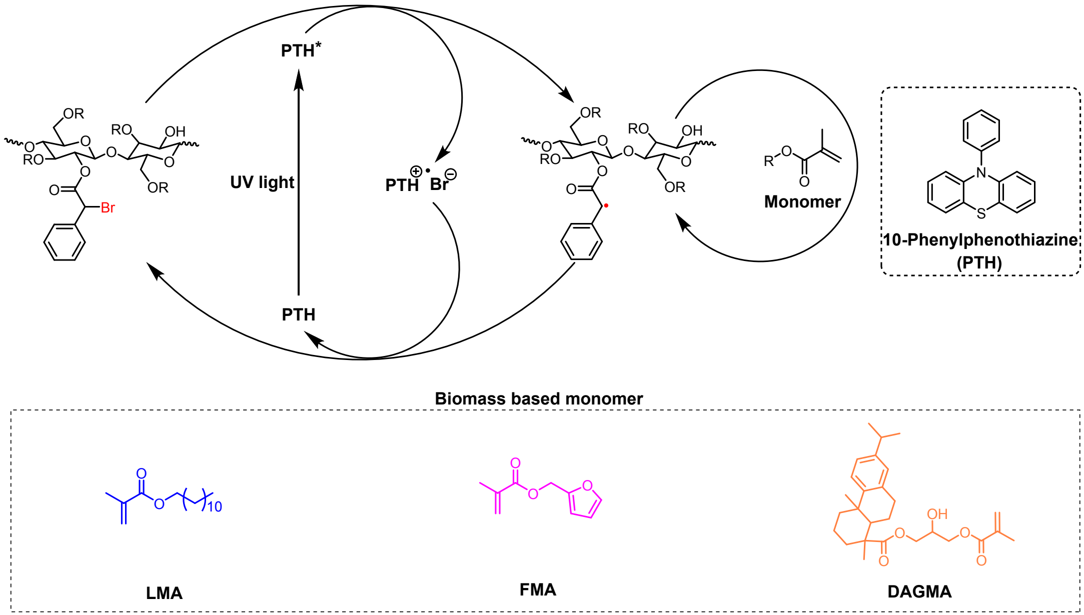
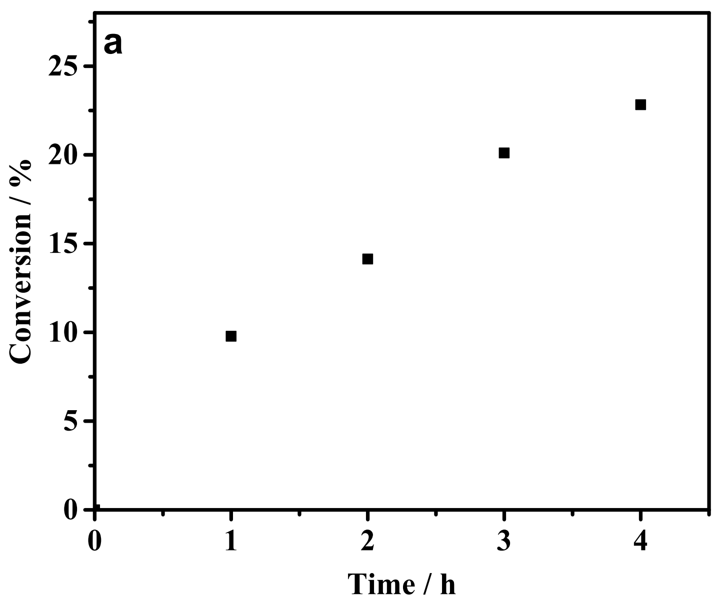


Fig.S1 the mechanism of metal-free ATRP with 10-Phenylphenothiazine as catalyst.



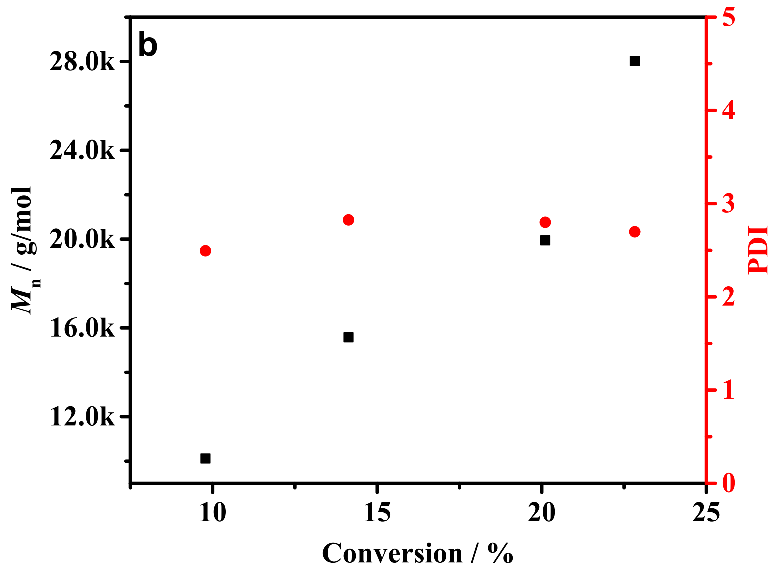


Fig.S2: Kinetic study of the metal-free ATRP of EC-*g*-$PLMA_{250}$ using EC-Br as initiator: (a) semilogarithmic kinetic plot; (b) number-average molecular weight (Mn) and dispersity (PDI) vs conversion.

Table S1: optimization of metal-free ATRP of FMA

Entry	Sample name	[I]:[M]:[PTH]	Time (h)	Conv [a] (%)	M_n [b] (g/mol)	PDI
1[a]	EC-*g*-$PFMA_{250}$	1:250:0.1	1.5	0	N/A	N/A
2[b]	EC-*g*-$PFMA_{250}$	1:250:0.1	1.5	14.7	12545	1.72
3c	EC-*g*-$PFMA_{250}$	1:250:0.1	1.5	8	9793	1.64

Reaction conditions: a: 35 ℃ without UV light, b: 35 ℃ with UV light, c: 25 ℃ with UV light.

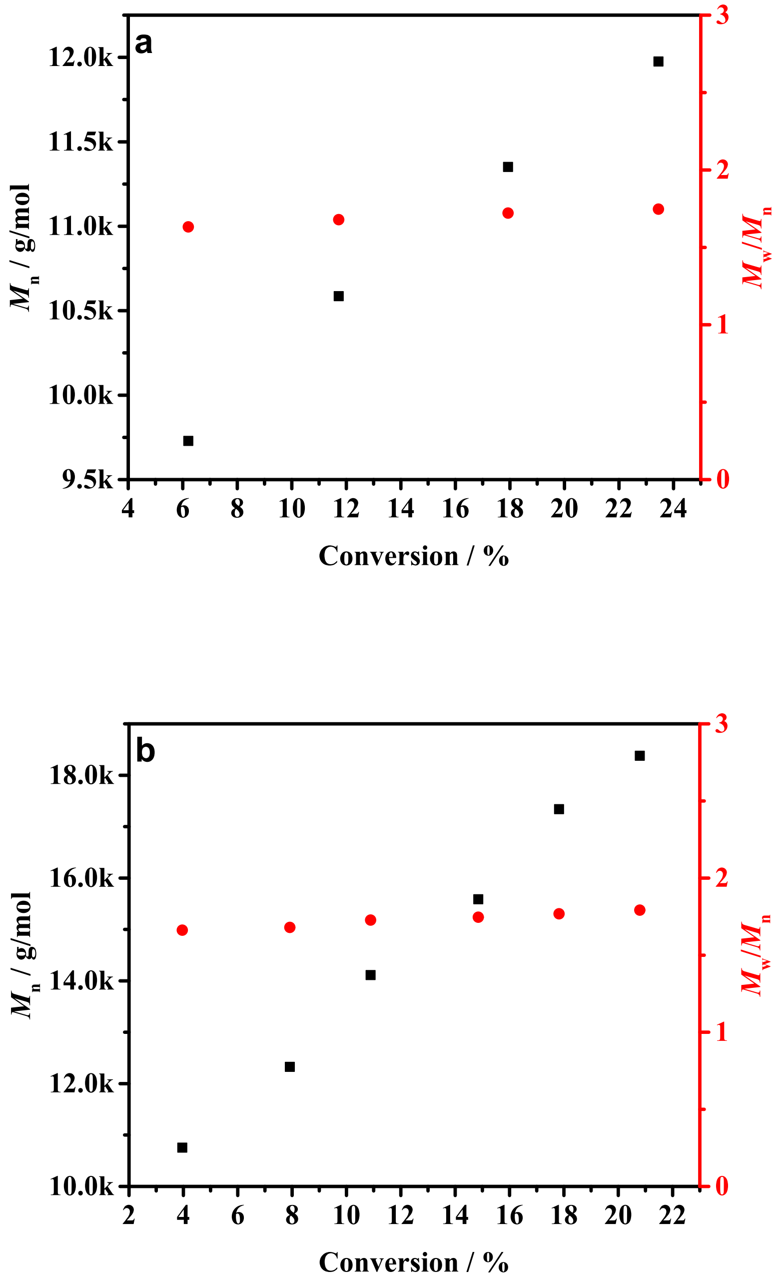


Fig.S3: Number-average molecular weight (M_n) and dispersity (PDI) vs conversion of the metal-free ATRP of (a) EC-*g*-$PFMA_{250}$, (b) EC-*g*-$PDAGMA_{250}$.

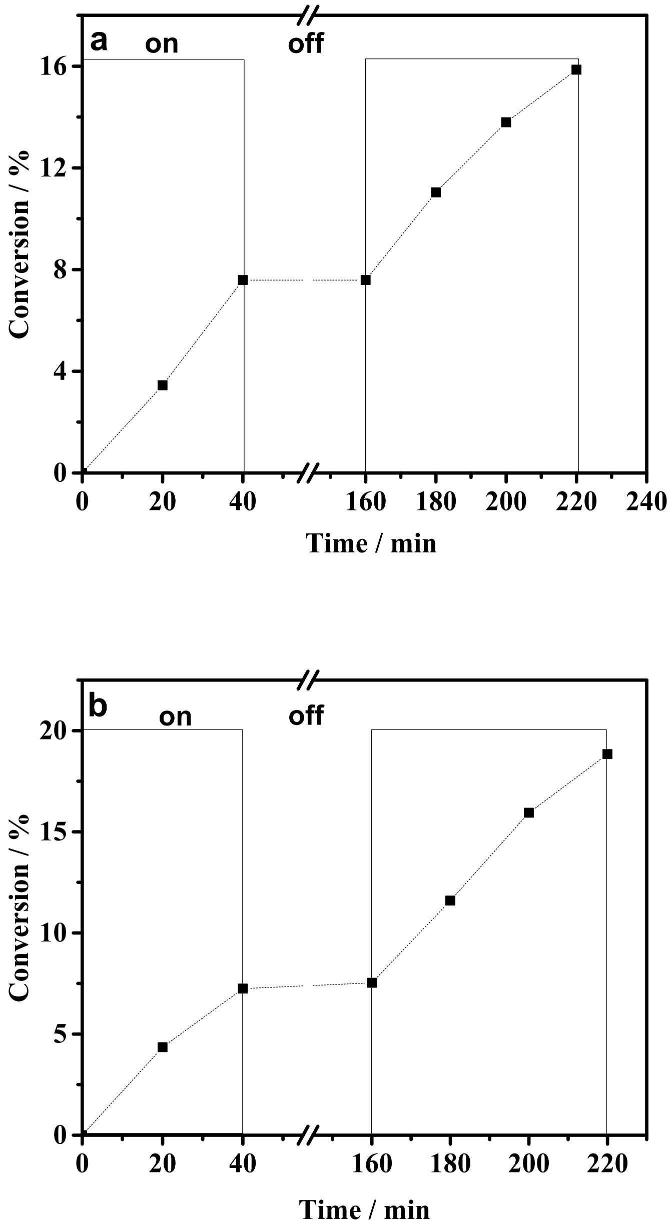


Fig.S4: Conversion vs time of metal-free ATRP with light "on-off" of (a) EC-*g*-$PFMA_{250}$, (b) EC-*g*-$PDAGMA_{250}$.

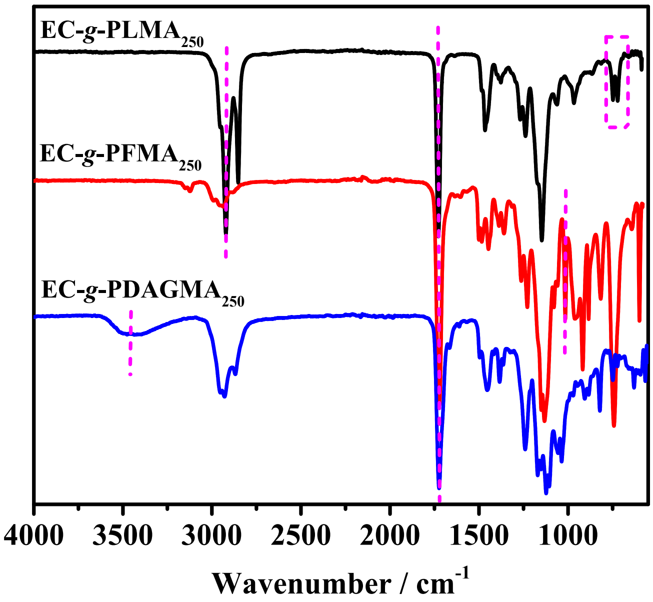
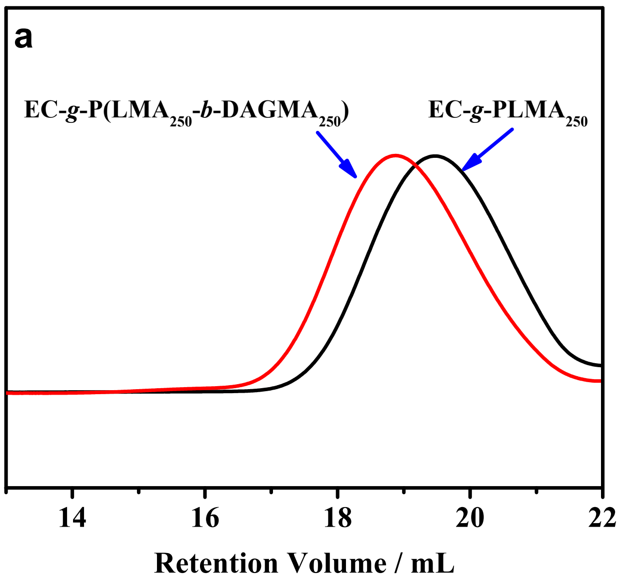


Fig.S5 FT-IR spectra EC-*g*-PLMA$_{250}$, EC-*g*-PFMA$_{250}$ and EC-*g*-PDAGMA$_{250}$.



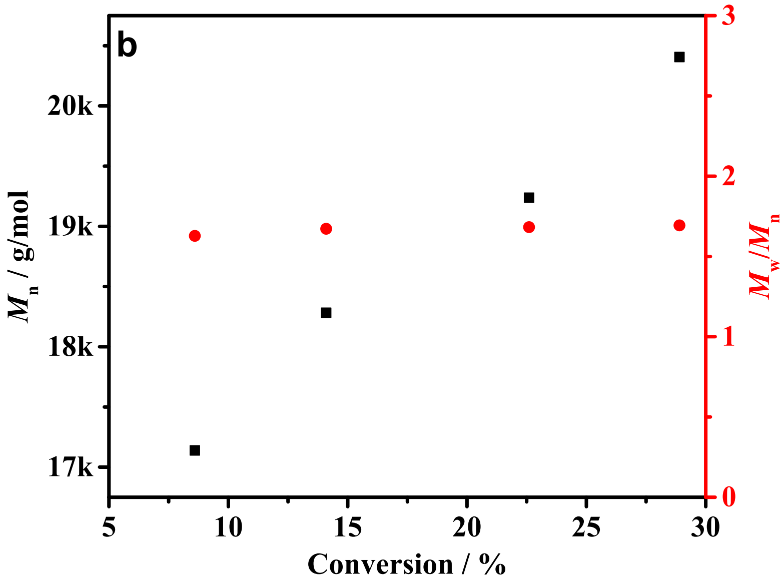


Fig.S6 Preparation of EC-*g*-P(LMA_{250}-*b*-$DAGMA_{250}$) by the chain extension: (a) GPC traces of EC graft copolymers before and after the chain extension; (b) number-average molecular weight and dispersity vs conversion.

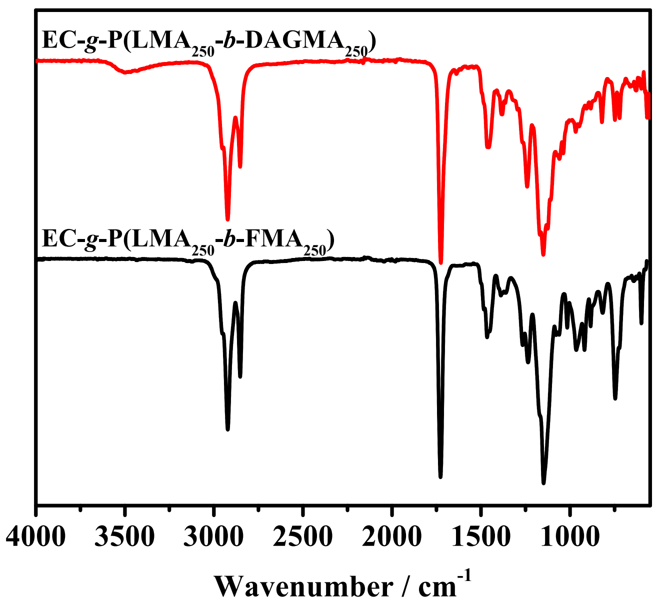


Fig.S7 FT-IR spectra of EC-*g*-P(LMA_{250}-*b*-FMA_{250}) and EC-*g*-P(LMA_{250}-*b*-$DAGMA_{250}$).

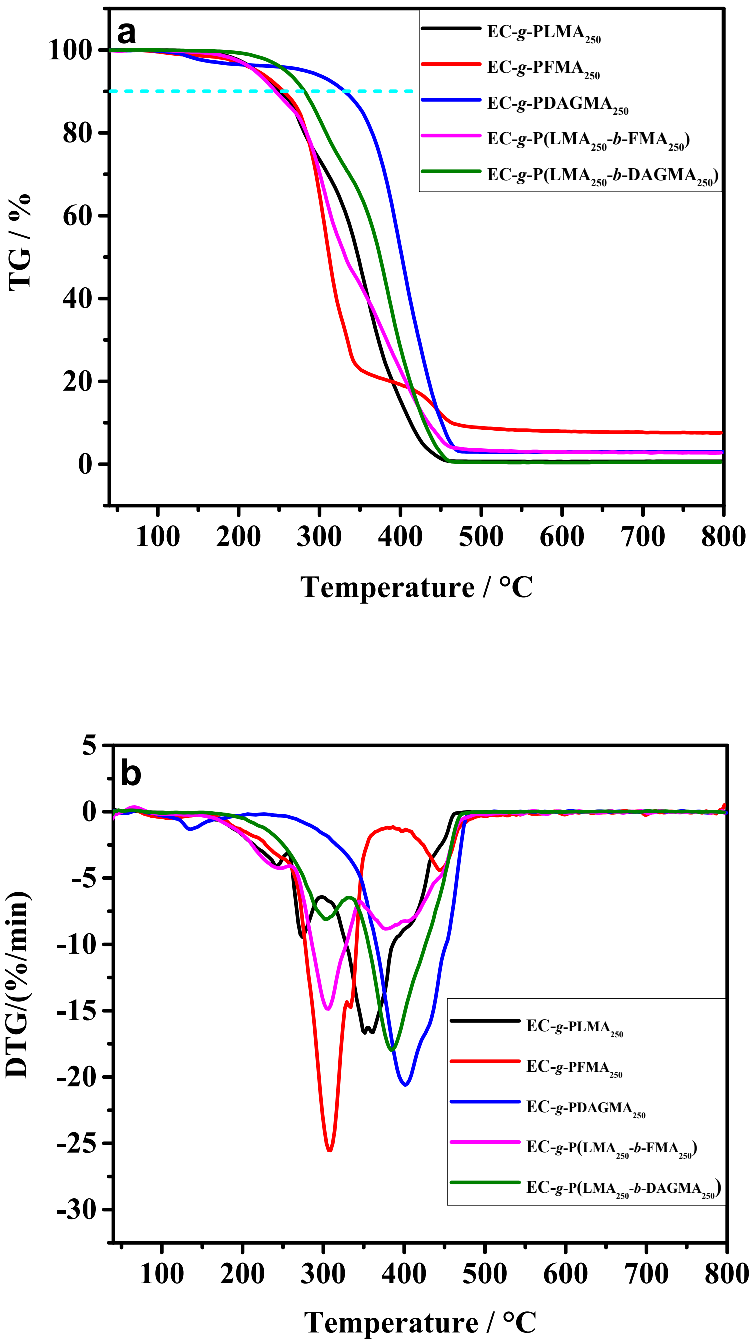


Fig.S8 (a) TG and (b) DTG curves for EC-*g*-$PLMA_{250}$, EC-*g*-$PFMA_{250}$, EC-*g*-$PDAGMA_{250}$ and EC-*g*-P(LMA_{250}-*b*-FMA_{250}) and EC-*g*-P(LMA_{250}-*b*-$DAGMA_{250}$).

Table S2: the data of $T_{d,10}$ and $T_{d,max}$ of EC graft copolymers

Sample name	$T_{d,10}$ / ℃	$T_{d,max}$ / ℃
EC-*g*-$PLMA_{250}$	249	360
EC-*g*-$PFMA_{250}$	254	307

EC-*g*-PDAGMA$_{250}$	330	401
EC-*g*-P(LMA$_{250}$-*b*-FMA$_{250}$)	245	305
EC-*g*-P(LMA$_{250}$-*b*-DAGMA$_{250}$)	281	385

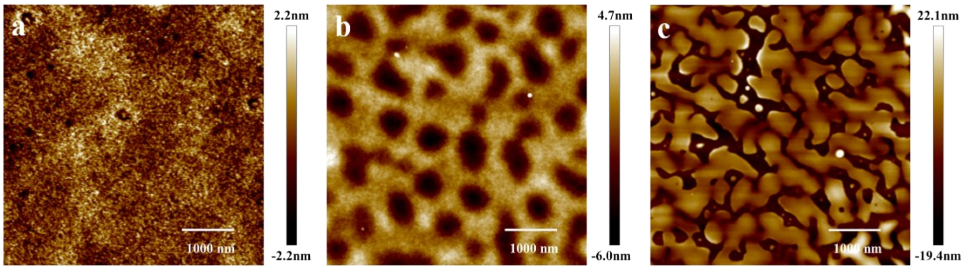


Fig.S9: AFM height images of (a) EC-*g*-PLMA$_{250}$, (b) EC-*g*-PFMA$_{250}$, (c) EC-*g*-PDAGMA$_{250}$.

Atom economy was defined in Equation S**1,** where M_{input} is the molecular weight of chemicals input to all reactions and $M_{product}$ is the molecular weight of desired chemical product[2].

$$atom\ economy = \frac{M_{product}}{M_{input}} \times 100\% \quad (S1)$$

During the synthesis process of EC-B-Br, we defined one D-glucose as a unit. The M_{input} of the synthetic EC-B-Br was 522.15, the $M_{product}$ was 377.19. So, the atom economy of the synthesis of EC-B-Br was 72.2 %.

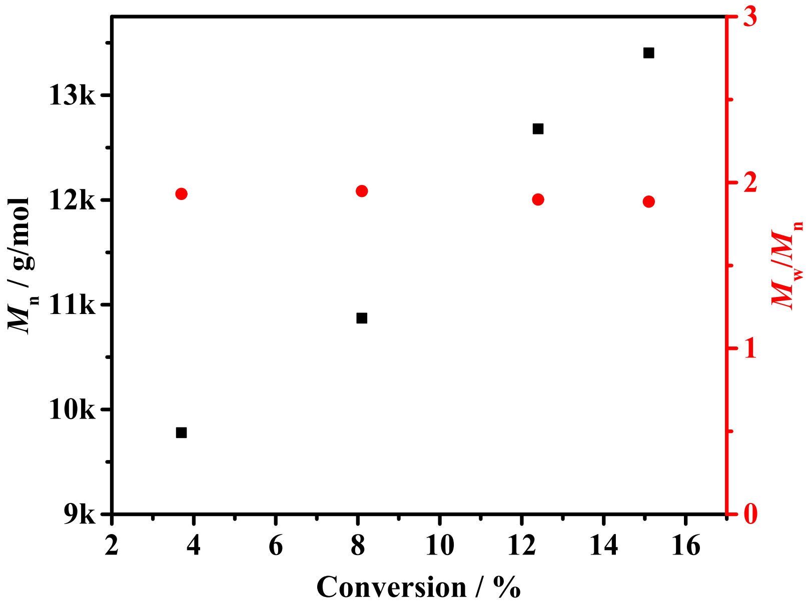


Fig.S10: Number-average molecular weight (M_n) and dispersity (PDI) vs conversion of the metal-free ATRP of EC-*g*-PLMA in solvent-free systems.

Reference

1. J. Yu, Y. Liu, X. Liu, C. Wang, J. Wang, F. Chu and C. Tang, *Green Chemistry*, 2014, **16**, 1854-1864.
2. B. M. Trost, *Angewandte Chemie International Edition in English*, 1995, **34**, 259-281.