Supplementary Information

Iodine-mediated photocontrolled atom transfer radical polymerization (photo-ATRP) and block polymerization combined with ring-opening polymerization (ROP) via a superbase

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1. Supporting data

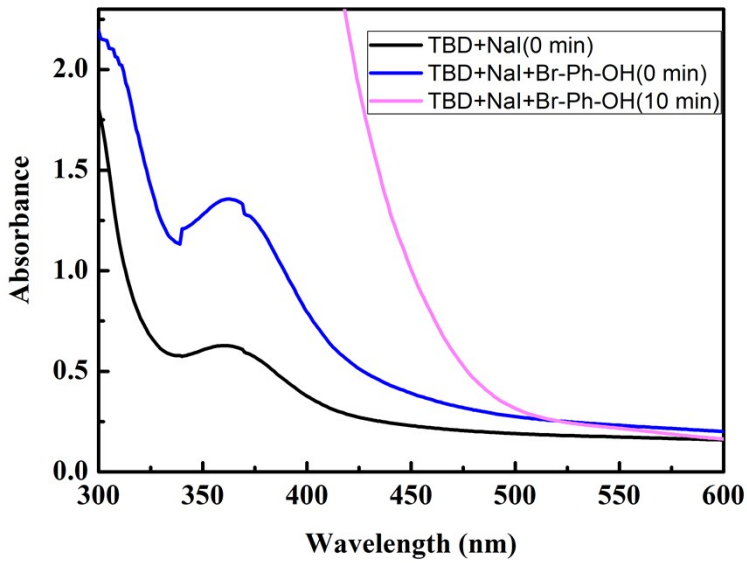

Fig. S1 UV-vis spectra of TBD (0.02 mmol) with NaI (0.021 mmol) (black line), then Br-Ph-OH (0.02 mmol) was added to this solution (blue line) and irradiated with a white LED for 10 min (pink line). Solvent: MMA.

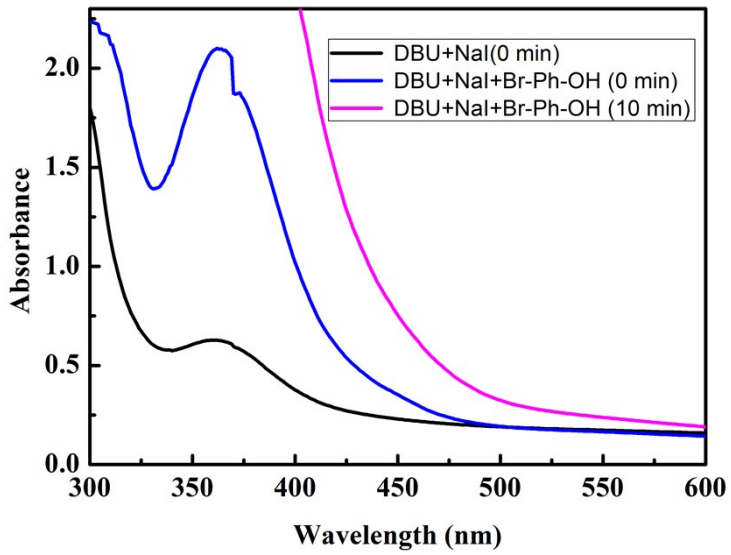

Fig. S2 UV-vis spectra of DBU (0.02 mmol) with NaI (0.021 mmol) (black line), then Br-Ph-OH (0.02 mmol) was added to this solution (blue line) and irradiated with a white LED for 10 min (pink line). Solvent: MMA.

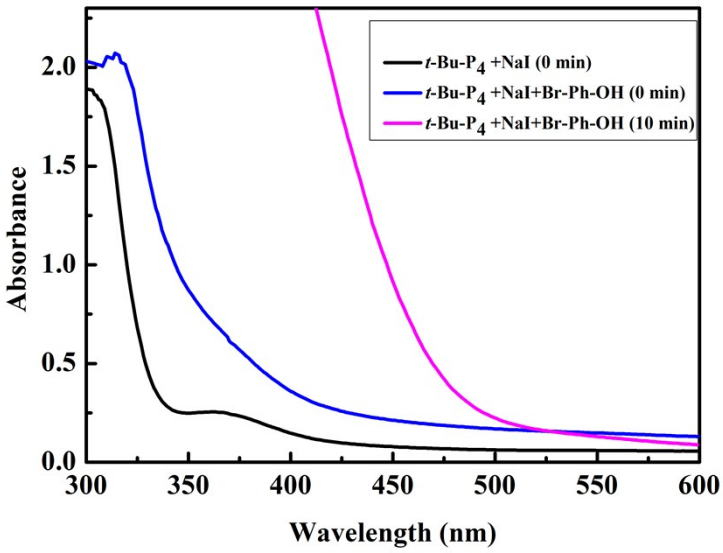

Fig. S3 UV-vis spectra of *t*-Bu-P_4 (0.02 mmol) with NaI (0.021 mmol) (black line), then Br-Ph-OH (0.02 mmol) was added to this solution (blue line) and irradiated with a white LED for 10 min (pink line). Solvent: MMA.

Table S1. Preparation of PMMA by iodine-mediated photo-ATRP under white LED irradiation (dark condition data in Fig. 2a).

Entry	Monomer	Catalyst	$[MMA]_0/[_L\text{-}LA]_0/[Br\text{-}Ph\text{-}OH]_0/[NaI]_0/[Catalyst]_0$ (mM)	t (h)	Conv.[b] (%)	M_n[d] ($M_{n,theo}$)[e]	PDI
	MMA	TMG	100:0:1:1.025:1	0.5-1	30	4,800 (3,000)	1.6
				1.5-2	47	5,900 (4,700)	1.5
				2.5-3	60.5	7,500 (6,100)	1.39

Experimental conditions: see Table 1.

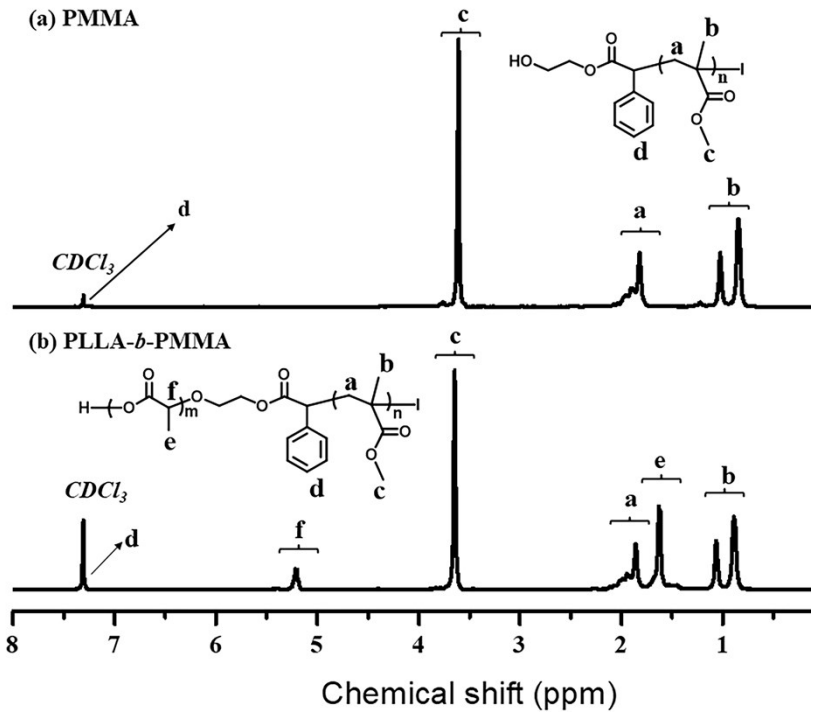

Fig.S4 (a) ^{1}H NMR spectrum (in $CDCl_3$) of PMMA and (b) PMMA-*b*-PLLA (entry 4, Table1).

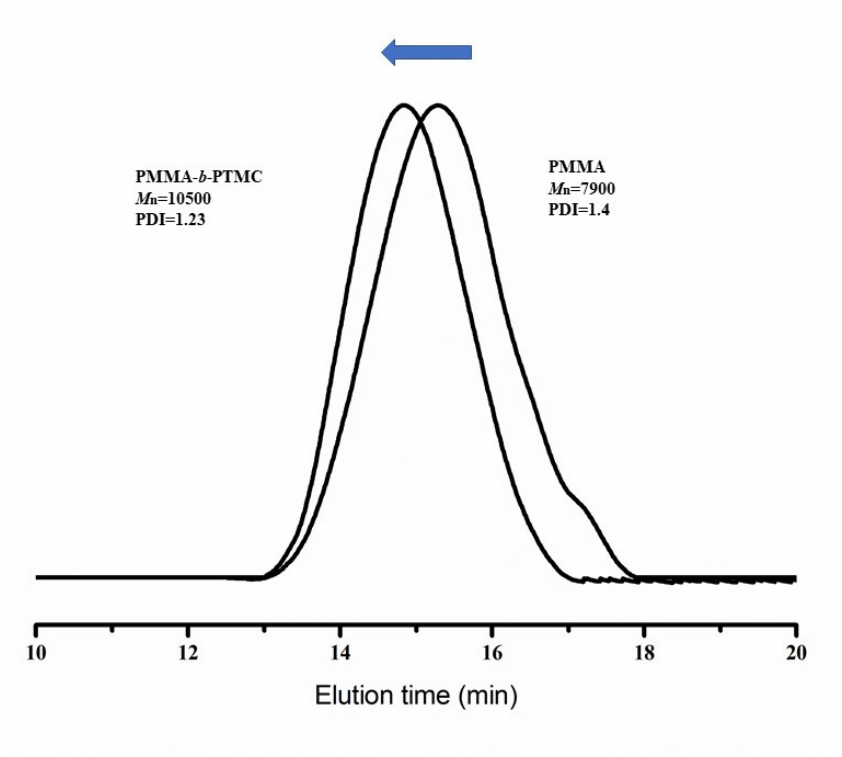

Fig.S5 GPC traces of PMMA and PMMA-*b*-PTMC (entry 1, Table 2).

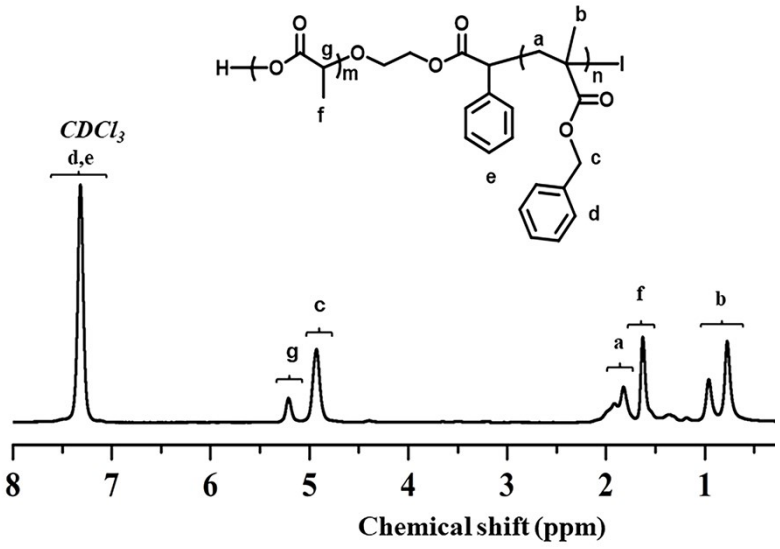

Fig.S6 ^{1}H NMR spectrum of PBzMA-*b*-PLLA (entry 2, Table 2).

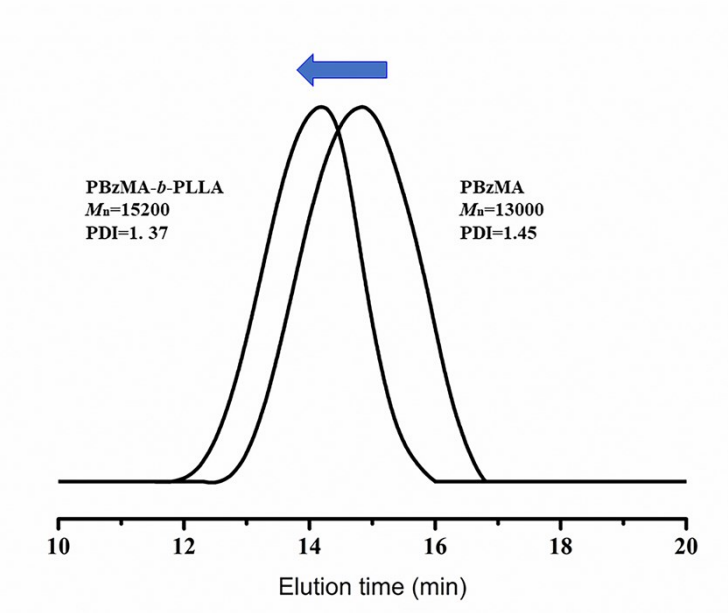

Fig.S7 GPC traces of PBzMA and PBzMA-*b*-PLLA (entry 2, Table 2).

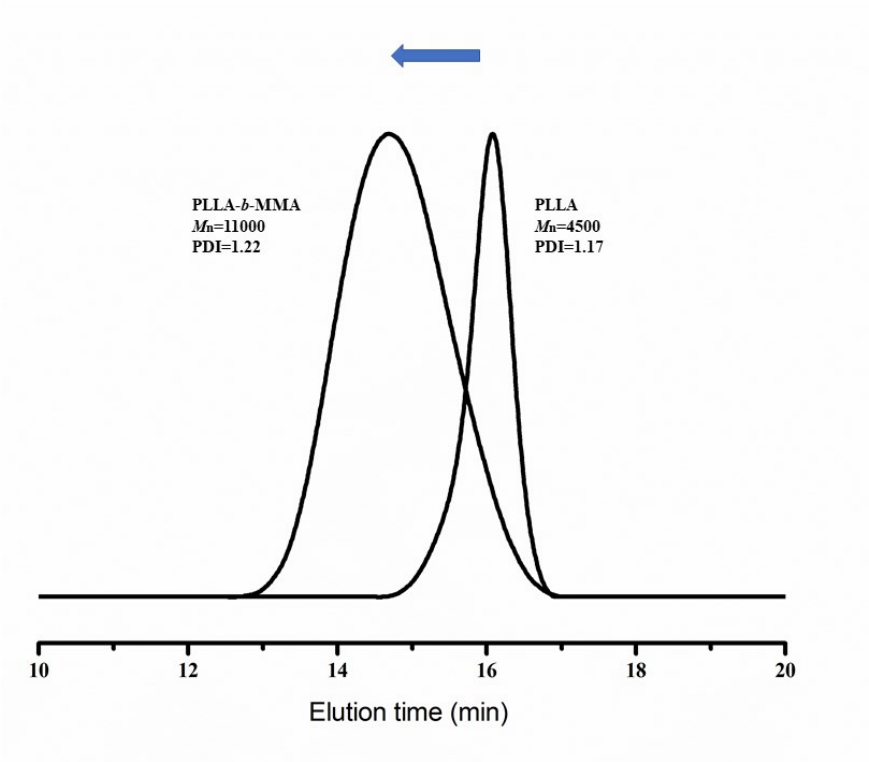

Fig.S8 GPC traces of PLLA and PLLA-*b*-PMMA (entry 3, Table 2).

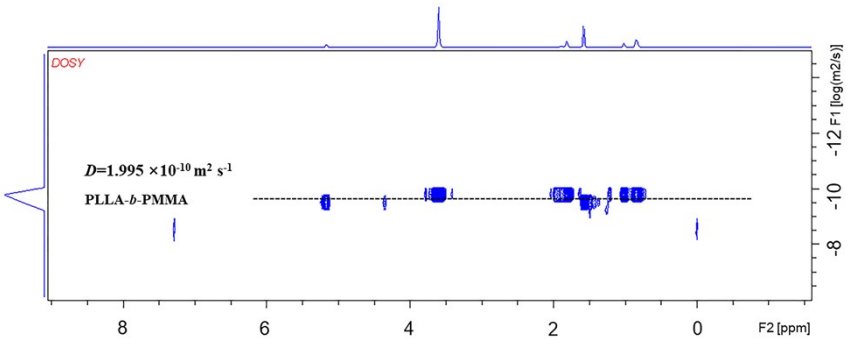

Fig.S9 DOSY ^{1}H NMR spectrum (recorded in $CDCl_3$) of a PLLA-*b*-PMMA (entry 3, Table 2) obtained in a "one-pot" process.

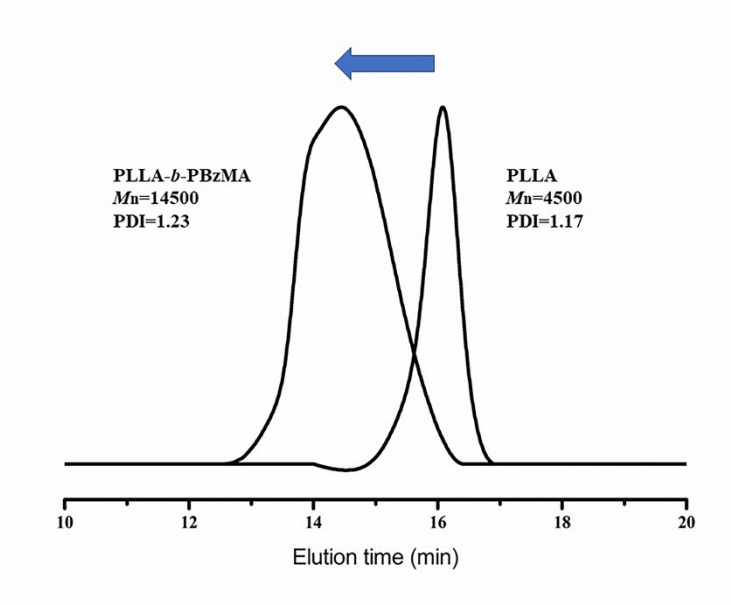

Fig.S10 GPC traces of PLLA and PLLA-*b*-PBzMA (entry 4, Table 2).

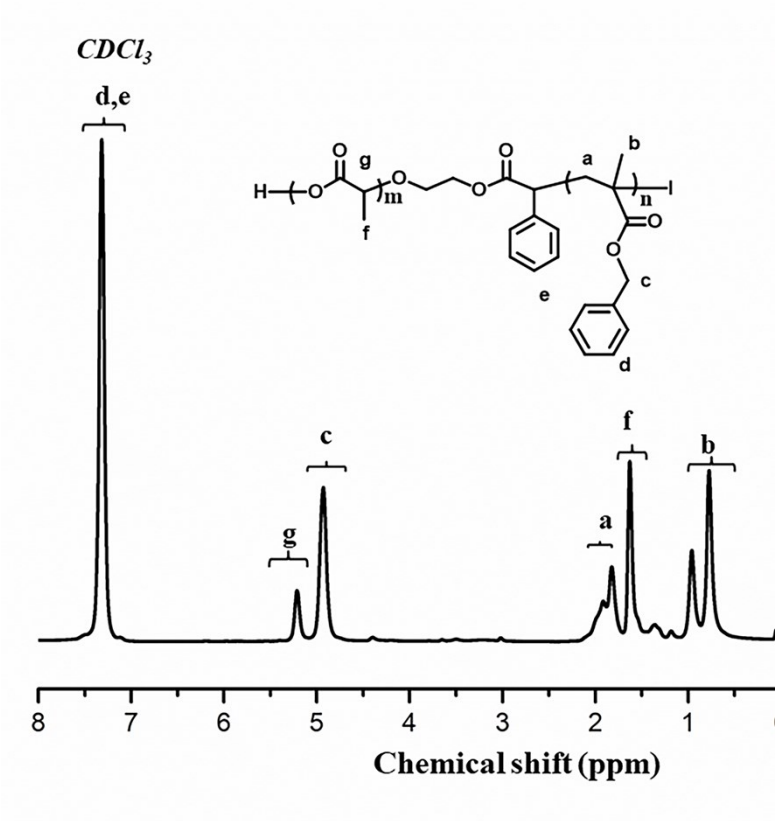

Fig.S11 ^{1}H NMR spectrum of PLLA-*b*-PBzMA (entry 4, Table 2).