Electronic Supplementary Information

Ultrafast, Green and Recyclable PhotoRDRP in Ionic Liquid Towards Multi-stimuli Responsive Amphiphilic Copolymers

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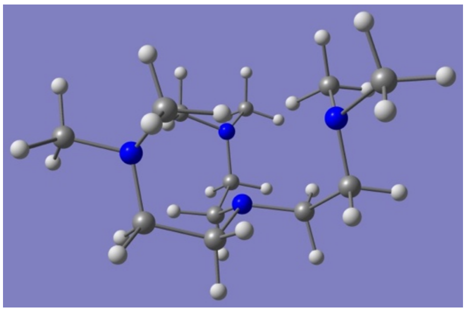
Computaional details

[Me_6TREN]$^{+•}$, Charge = +1, Multiplicity = 2, optimized coordinates



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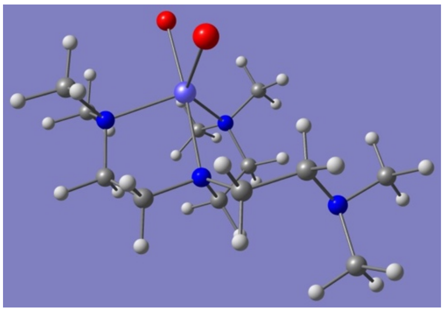

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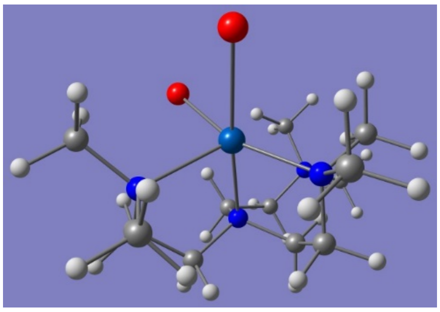

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H	-2.769617000	1.261501000	5.754626000
H	-4.183199000	0.682558000	4.797876000
H	-2.858392000	-0.441971000	5.157870000
Co	-2.855947000	-0.469995000	1.980876000
Br	-2.530227000	-2.414756000	3.386690000
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B. Supporting tables and Figures

Table S1 Reaction conditions and results for the alloy-mediated ambient temperature photoRDRP of GMA in ionic liquid using EBiB as the initiator.[a]

Entry	Reaction condition	Time (min)	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P1	GMA/EBiB/Ni-Co/bpy	120	0	-	-	-
P2	GMA/EBiB/Ni-Co/PMDETA	120	32	9300	8800	1.46
P3	GMA/EBiB/Ni-Co/Me_6TREN	20	100	28600	27700	1.17
P4	GMA/Ni-Co/Me_6TREN	120	7	-	13100	2.11
P5	GMA/EBiB/ Me_6TREN	120	19	8200	17300	1.98
P6	GMA/EBiB/Ni-Co	120	0	-	-	-

[a]Reaction Conditions: $[GMA]_0/[EBiB]_0 = 200$. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([GMA]_0/[EBiB]_0 \times \text{yield} \times M_{GMA}) + M_{EBiB}$, where M_{GMA} (= 142.15 g mol^{-1}) and M_{EBiB} (= 195.05 g mol^{-1}) are the molecular weight of GMA and EBiB, respectively. [d]Obtained from SEC measurements.

Table S2. Reaction conditions and results for the effect of varying $[GMA]_0/[EBiB]_0$ on the alloy-mediated ambient temperature photoRDRP of GMA in ionic liquid using EBiB as the initiator.[a]

Entry	$[GMA]_0/[EBiB]_0$	Conv.[b] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P7	10	100	1600	1900	1.19
P8	25	100	3700	3300	1.17
P9	50	100	7300	6900	1.15
P10	100	100	14400	13800	1.16
P11	150	100	21500	22500	1.18
P12	200	100	28600	27700	1.17

[a]Reaction Conditions: reaction time = 20 min. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([GMA]_0/[EBiB]_0 \times \text{yield} \times M_{GMA}) + M_{EBiB}$, where M_{GMA} (= 142.15 g mol^{-1}) and M_{EBiB} (= 195.05 g mol^{-1}) are the molecular weight of GMA and EBiB, respectively. [d]Obtained from SEC measurements.

Table S3. Reaction conditions and results for the catalyst recyclability study of alloy-mediated ambient temperature photoRDRP of GMA in ionic liquid using EBiB as the initiator.[a]

Entry	Cycle	Conv.[a] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P13	First	100	28600	28100	1.18
P14	Second	100	28600	27900	1.17
P15	Third	100	28600	28400	1.20
P16	Fourth	100	28600	28000	1.18

[a]Reaction Conditions: $[GMA]_0/[EBiB]_0 = 200$. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([GMA]_0/[EBiB]_0 \times \text{yield} \times M_{GMA}) + M_{EBiB}$, where M_{GMA} (= 142.15 g mol^{-1}) and M_{EBiB} (= 195.05 g mol^{-1}) are the molecular weight of GMA and EBiB, respectively. [d]Obtained from SEC measurements.

Table S4. Reaction conditions and results for the IL recyclability study of alloy-mediated ambient temperature photoRDRP of GMA in ionic liquid using EBiB as the initiator.[a]

Entry	Extraction (min)	Conv.[a] (%)	$M_{n,theo.}$[c] (g mol^{-1})	$M_{n,SEC}$[d] (g mol^{-1})	$Đ$[d]
P17	1st	100	28600	28100	1.18
P18	2nd	100	28600	27700	1.17
P19	3rd	100	28600	28800	1.16

[a]Reaction Conditions: $[GMA]_0/[EBiB]_0 = 200$. [b]Determined gravimetrically based on monomer feed. [c]Calculated using yield as conversion and the following equation: $M_{n,theo} = ([GMA]_0/[EBiB]_0 \times \text{yield} \times M_{GMA}) + M_{EBiB}$, where M_{GMA} (= 142.15 g mol^{-1}) and M_{EBiB} (= 195.05 g mol^{-1}) are the molecular weight of GMA and EBiB, respectively. [d]Obtained from SEC measurements.

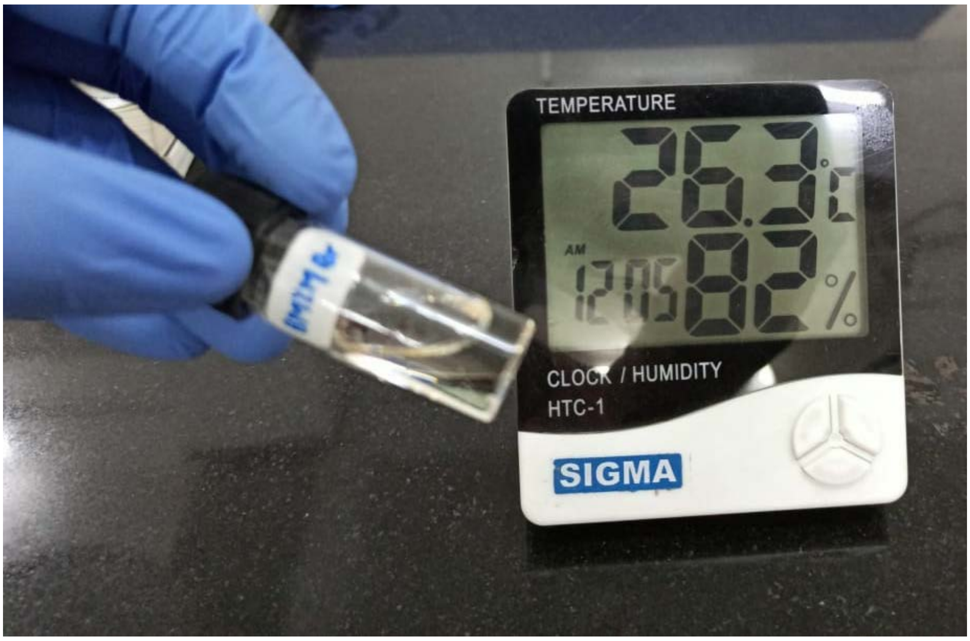

Fig. S1 Representative image of the ionic liquid, BMIMBr at ambient temperature.

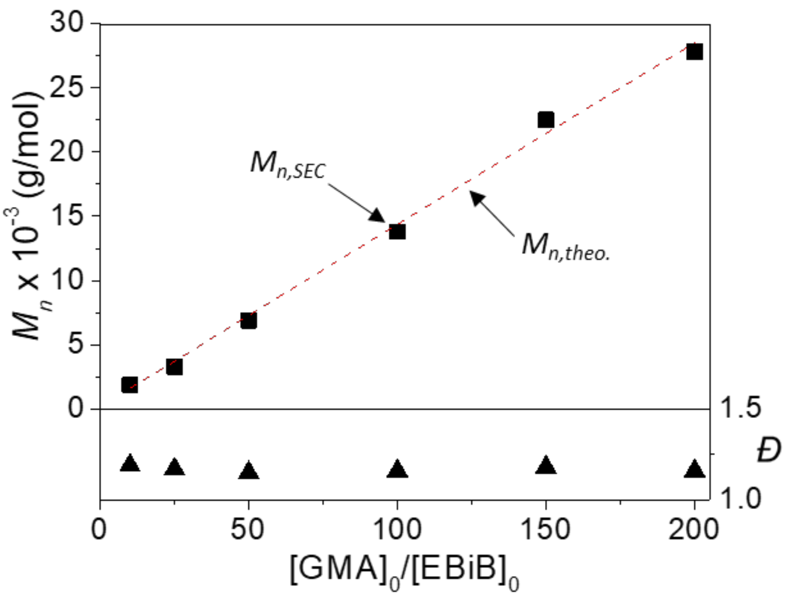

Fig. S2 Evolution of M_n and $Đ$ with increasing $[GMA]_0/[EBiB]_0$ for recyclable alloy-mediated ambient temperature photoRDRP in ionic liquid using EBiB as the initiator (P7–P12, Table S2).

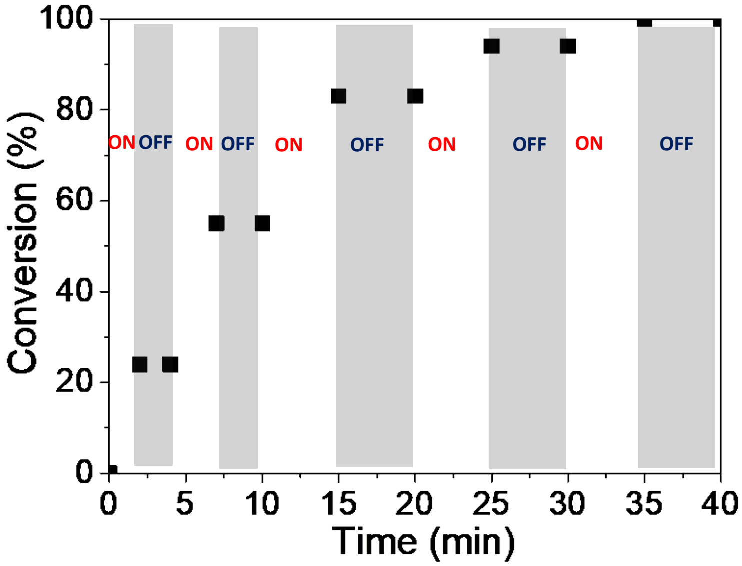

Fig. S3 Evidence of temporal control via consecutive light (white area) and dark (shaded area) exposure for recyclable alloy-mediated ambient temperature photoRDRP in ionic liquid using EBiB as the initiator.

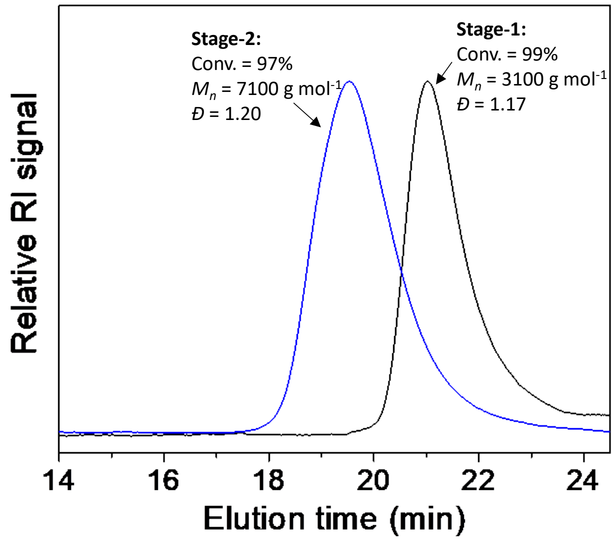

Fig. S4 Evolution of SEC traces along with M_n and $Đ$ values during *in situ* chain extension for alloy-mediated ambient temperature photoRDRP of GMA in ionic liquid using EBiB as the initiator.

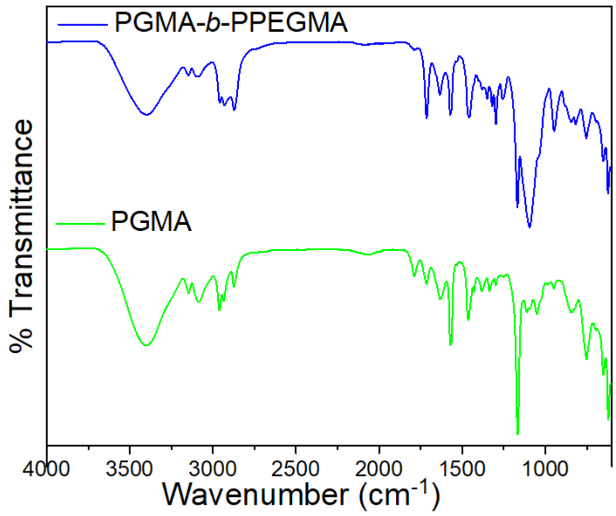

Fig. S5 ATR-IR spectra of PGMA-Br macroinitiator (a) and PGMA-*b*-PPEGMA.

Strong peaks at 1285 cm^{-1} and 842 cm^{-1} suggested the presence of the epoxy groups of GMA. The C=O stretching peak at 1718 cm^{-1} emerged due to the introduction of ester-containing PEGMA, while C-O-C at 1094 cm^{-1} peaks increased, revealing the success of the block copolymer formation with PGMA.[1]

D. References.

1. Z. Cheng, X. Zhu, E. Kang and K. Neoh, *Langmuir*, 2005, **21**, 7180-7185.