

Supporting information

for

Photo-Induced Iron-Catalyzed ATRP of Renewable Monomers in Low-Toxicity Solvents: A Greener Approach

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Experimental

1. Materials

Methyl α -bromophenylacetate, (MBPA, > 97.0%) and Guaiacol (>98%) were procured from Tokyo Chemical Industries. Iron(III) bromide anhydrous, (FeBr_3) was bought from ABCR (abcr GmbH). Ethyl acetate ($\geq 99.5\%$) and sodium hydrogen carbonate (NaHCO_3 , $\geq 99.7\%$) were obtained from Fisher Scientific. Thymol (98+%) was supplied by Alfa Aesar. Vanillin ($\geq 99\%$) was fabricated by ROTH. All the other chemicals were procured from Sigma Aldrich. The blue ECO LED strip light (48 W, $\lambda = 465\text{nm}$ (+/-5nm), 16.4' Spool, 36 SMD 3528 LED's/Foot) was purchased from solid Apollo Led.

2. Instrumentation

2.1 ^1H nuclear magnetic resonance (NMR) spectra were measured in CDCl_3 (99.8 %, ReseaChem) on a Bruker Avance-300 spectrometer. Chemical shifts are given in ppm and are referenced to residual solvent proton signals.

2.2 Size-exclusion chromatography (SEC) was measured on Shimadzu equipment comprising a CBM-20A system controller, an LC-20AD pump (flow rate at 1 mL min^{-1}), a SIL-20A automatic injector, a $10.0\ \mu\text{m}$ bead-size guard column ($50 \times 7.5\text{ mm}$) followed by three KF-805L columns ($300 \times 8\text{ mm}$, bead size: $10\ \mu\text{m}$, pore size maximum: $5000\ \text{\AA}$), an SPD-20A ultraviolet detector, and an RID-20A *differential refractive index detector*. The columns' temperature was maintained at $40\ ^\circ\text{C}$ using a CTO-20A oven. *N,N*-dimethylacetamide was used as eluent (HPLC grade, Acros, with 0.03% w/v LiBr). Molecular weights were determined according to calibration with commercial narrow molar mass distribution

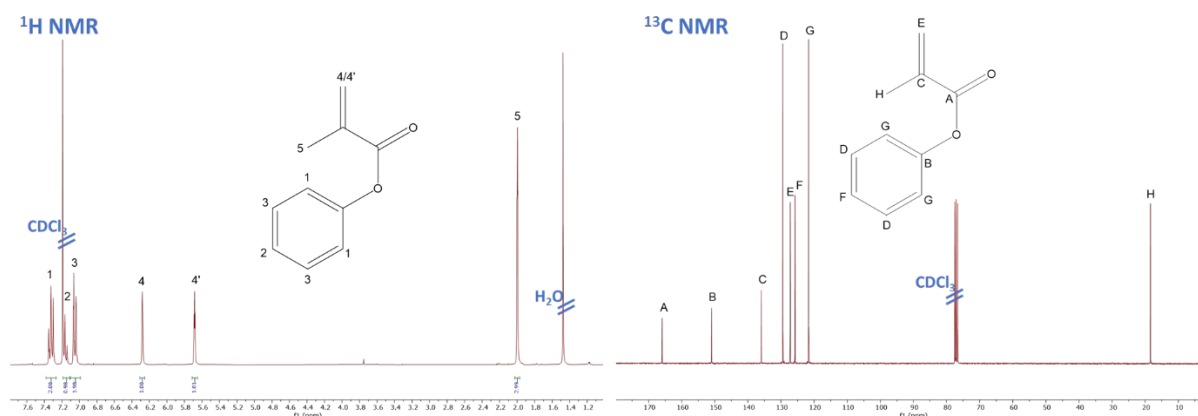
poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5×10^6 g mol⁻¹ (Agilent technology). Before injection, all samples were passed through 0.45 μ m filters.

3. Synthetic procedures

3.1 Monomer synthesis

3.1.1 Phenyl Methacrylate (PheMA):

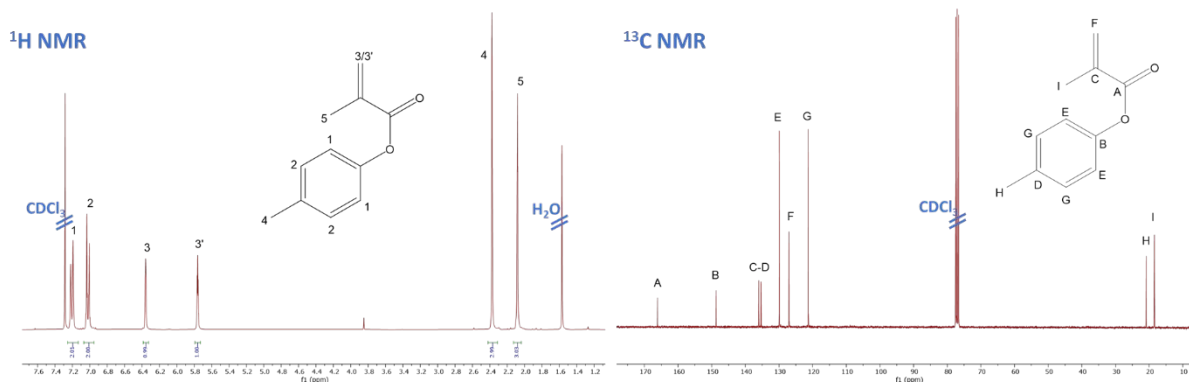
Phenol (37.09 g, 0.39 mol, 1 equiv.), 2-methyltetrahydrofuran (100 mL) and TEA (60.42 mL, 0.43 mol, 1.1 equiv.) were mixed in a 250 mL round bottom flask. Methacrylic anhydride (64.57 mL, 0.43 mol, 1.1 equiv.) was added and the solution was stirred at 40 °C overnight. Methacrylic acid was eliminated by extracting the organic phase four times with a saturated NaHCO₃ solution. Subsequently the organic phase was dried with anhydrous MgSO₄, filtered and the solvent was removed in the rotary evaporator. Purification was conducted by column chromatography with petroleum ether/ethylacetate (90/10 v/v) as the mobile phase. Evaporation of the solvents led to a clear, viscous liquid (41.1 g, 65% yield).



Spectrum 1: ¹H and ¹³C NMR analysis of PheMA

3.1.2 Cresol Methacrylate (CreMA):

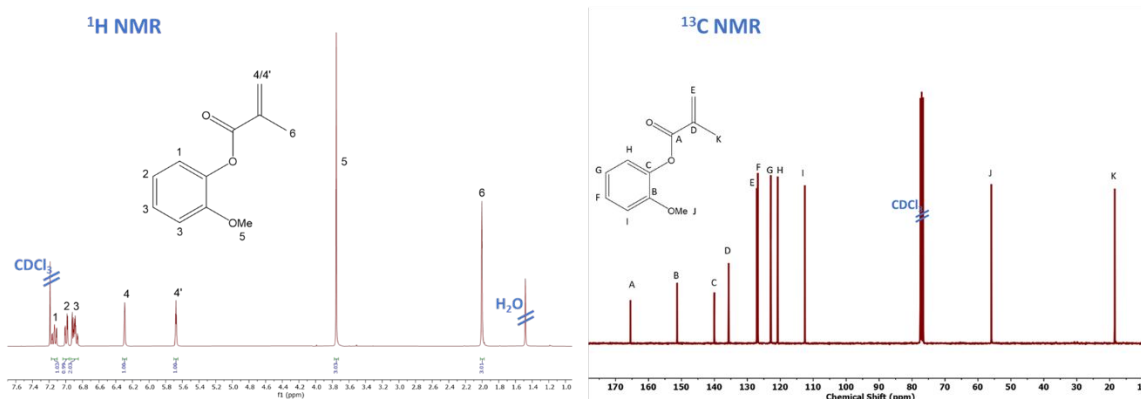
The *p*-Cresol (36.44 g, 0.34 mol, 1 equiv.), 2-methyltetrahydrofuran (100 mL) and TEA (51.66 mL, 0.37 mol, 1.1 equiv.) were mixed in a 250 mL round bottom flask. Methacrylic anhydride (55.21 mL, 0.37 mol, 1.1 equiv.) was added and the solution was stirred at 40 °C overnight. Methacrylic acid was eliminated by extracting the organic phase three times with a saturated sodium bicarbonate (NaHCO₃) solution (2x), followed by 0.5M NaOH (3x) and once again NaHCO₃ solution. Subsequently the organic phase was dried with anhydrous magnesium sulphate (MgSO₄), filtered and the solvent was removed in the rotary evaporator. After this procedure a yellowish liquid was obtained. Purification of the crude product was conducted by column chromatography with petroleum ether/ethylacetate (95/5 v/v) as the mobile phase. Evaporation of the solvents led to the product as a clear liquid (39.36 g, 66% yield).



Spectrum 2: ^1H and ^{13}C NMR analysis of CreMA

3.1.3 Guaiacol Methacrylate (GuMA):

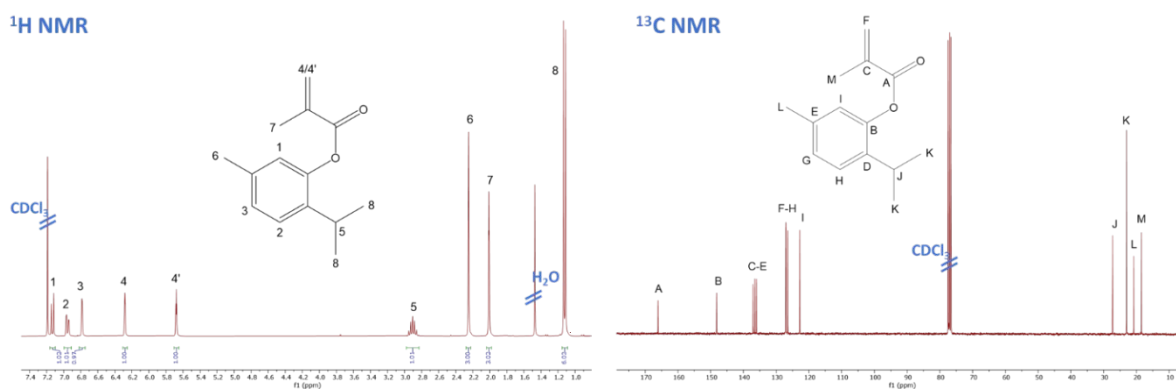
Guaiacol (37.6 g, 0.3 mol, 1 equiv.), 2-methyltetrahydrofuran (100 mL) and TEA (46.44 mL, 0.33 mol, 1,1 equiv.) were mixed in a dried 250 mL round bottom flask. Methacrylic anhydride (49.62 mL, 0.33 mol, 1,1 equiv.) was added and the solution was stirred at 40 °C overnight. Methacrylic acid was eliminated by extracting the organic phase two times with a saturated sodium bicarbonate (NaHCO_3) solution, followed by extraction with 0.5M NaOH (3x) and once again NaHCO_3 solution. Subsequently the organic phase was dried with anhydrous magnesium sulfate (MgSO_4), filtered and the solvent was removed in the rotary evaporator. Purification was conducted by column chromatography with petroleum ether/ethyl acetate (85/15 v/v) as the mobile phase. Evaporation of the solvents led to a clear liquid (35.6 g, 60% yield).



Spectrum 3: ^1H and ^{13}C NMR analysis of GuMA

3.1.4 Thymol Methacrylate (ThyMA):

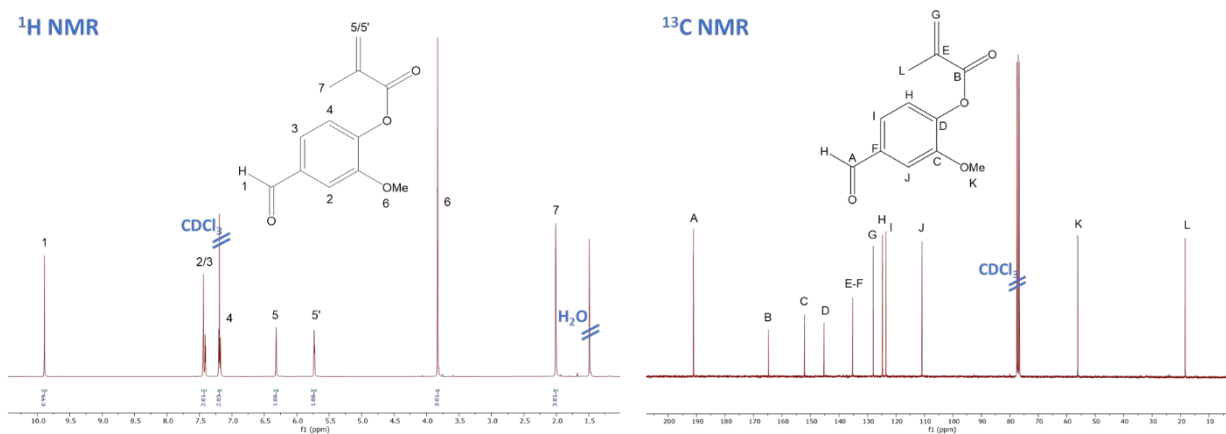
Thymol (30.00 g, 0.2 mol), 2-methyltetrahydrofuran (85.71 mL) and TEA (30.62 mL, 0.22 mmol, 1.1 equiv.) were mixed in a dried 250 mL round bottom flask. Methacrylic anhydride (32.74 mL, 0.22 mmol, 1.1 equiv.) was added and the solution was stirred at 40 °C overnight. The crude product was filtered in order to remove the triethylammonium salt and washed with diethyl ether. Methacrylic acid was eliminated by extracting the organic phase three times with a saturated sodium bicarbonate (NaHCO₃) solution. Subsequently the organic phase was dried with anhydrous magnesium sulfate (MgSO₄), filtered and the solvent was removed in the rotary evaporator under reducing pressure. Purification was conducted by column chromatography with petroleum ether/ethyl acetate (96/4 v/v) as the mobile phase. Evaporation of the solvents led to a clear, viscous oil (23.84 g, 55% yield).



Spectrum 4: ¹H and ¹³C NMR analysis of ThyMA

3.1.5 Vanillin Methacrylate (VaMA):

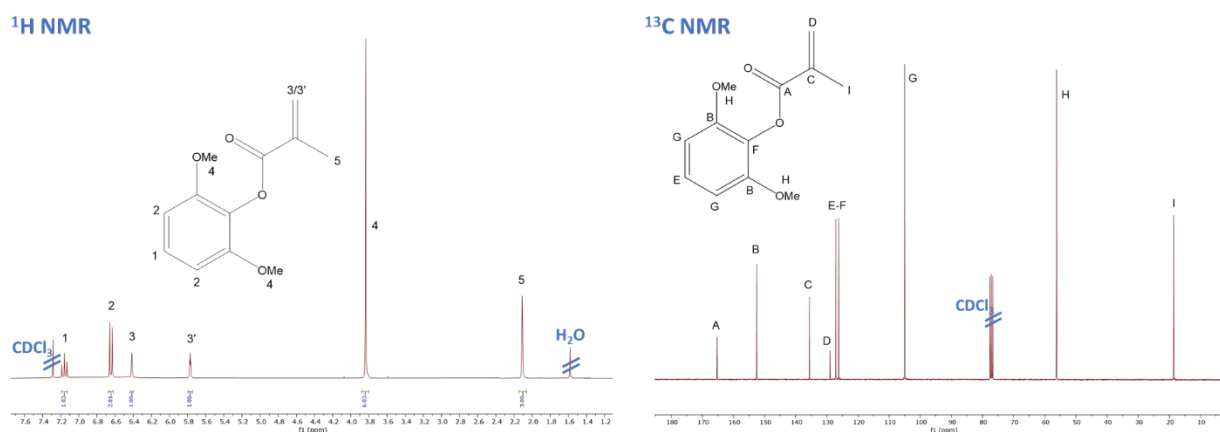
Vanillin (35.00 g, 0.23 mol, 1equiv.), 2-methyltetrahydrofuran (100 mL) and TEA (35.27 mL, 0.25 mol, 1.1 equiv.) were mixed in a 250 mL round bottom flask. Methacrylic anhydride (37.69 mL, 0.25 mol, 1.1 equiv.) was added and the solution was stirred at 40 °C overnight. Methacrylic acid was eliminated by extracting the organic phase with water and with a saturated NaHCO₃ solution (2x) followed by extraction with 0.5M NaOH (2x), brine (saturated NaCl solution) and water again. Subsequently the organic phase was dried with MgSO₄, filtered and the solvent was removed in the rotary evaporator. Obtained were white crystals that were dried in the vacuum oven (29.66 g, 59% yield).



Spectrum 5: ¹H and ¹³C NMR analysis of VaMA

3.1.6 Syringol Methacrylate (SyrMA):

Syringol (2,6-Dimethoxyphenol) (37.19 g, 0.24 mol, 1 equiv.), 2-methyltetrahydrofuran (106.25 mL) and TEA (36.98 mL, 0.26 mol, 1.1 equiv.) were mixed in a 250 mL round bottom flask. Methacrylic anhydride (39.52 mL, 0.26 mol, 1.1 equiv.) was added and the solution was stirred at 40 °C overnight. Methacrylic acid and unreacted starting material was eliminated by extracting the organic phase three times with a NaHCO₃ solution followed by 0.5M NaOH (3x). Subsequently the organic phase was dried with anhydrous MgSO₄, filtered and the solvent was removed in the rotary evaporator. After drying in the vacuum oven white crystals were obtained (33.6 g, 63% yield).



3.2 Photo-induced Iron-catalyzed ATRP:

3.2.1 General procedure for poly(PheMA) synthesis by Fe photo-ATRP:

TBABr (1.99 mg, 6.17*10⁻⁶ mol, 0.1 equiv.) and FeBr₃ (1.82 mg, 6.17*10⁻⁶ mol, 0.1 equiv.) were dissolved in tetraethylene glycol dimethyl ether (0.5 g) in a 4 mL glass vial. This solution is better to be prepared fresh for each experiment. Then, PheMA (0.5 g, 0.003 mol, 50 equiv.) was introduced, followed by MBPA (9.7 μL, 6.17*10⁻⁵ mol, 1 equiv.). The vial was sealed with a septum and was degassed by bubbling with nitrogen for 10 minutes under N₂ flow. Next, the vial was placed under a homemade LED strip blue light box (48 W, λ= 465 nm (+/-5nm)). The stirring rate for all experiments was fixed at 50 rpm. After the desired reaction time the polymerization was stopped by removing the vial from blue light irradiation and exposing the solution to air. It was sampled in order to determine the conversion *via* ¹H NMR. The molecular weight and dispersity were analyzed via SEC measurements (samples were passed through basic alumina to removed iron prior to SEC analysis).

The same procedure was followed for the other two solvents (2-methyltetrahydrofuran and cyclopentyl methyl ether).

For the polymerization of all the other monomers tetraethylene glycol dimethyl ether was used as a solvent under otherwise identical conditions as in the case of PheMA.

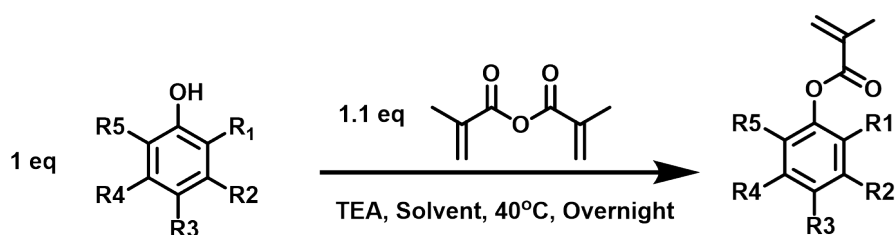
3.2.2 Procedure for P(PheMA-*b*-PheMA) block copolymer synthesis utilizing Fe photo-ATRP:

PPheMA macro-initiator crude mixture was diluted in acetone and passed through basic alumina to remove the Fe catalyst. Then the polymer was precipitated in methanol and dried in vacuum oven overnight.

Into a 4 mL glass vial, purified macro-initiator with $M_n = 6500$ and $\mathcal{D} = 1.17$ (50 mg, $7.7 \cdot 10^{-6}$, 1 equiv.) was dissolved in 1 mL of tetraethylene glycol dimethyl ether. PheMA (81.3 mg, $4.62 \cdot 10^{-4}$, 60 equiv.), FeBr_3 (0.45 mg, $1.5 \cdot 10^{-6}$, 0.2 equiv.) and TBABr (0.50 mg, $1.5 \cdot 10^{-6}$, 0.2 equiv.) and a stirrer bar were added to the vial and it was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 10 minutes. Next, the vial was placed under a homemade LED strip blue light box (48 W, $\lambda = 465\text{nm}$ ($\pm 5\text{nm}$)). The stirring rate for all experiments was fixed at 50 rpm. After the desired reaction time the polymerization was stopped by removing the vial from blue light irradiation and exposing the solution to air. It was sampled in order to determine the conversion *via* ^1H NMR. The molecular weight and dispersity were analysed via SEC measurements (samples were passed through basic alumina to removed iron prior to SEC analysis). Same procedure was followed for the synthesis of P(GuMA-*b*-PheMA) block copolymer.

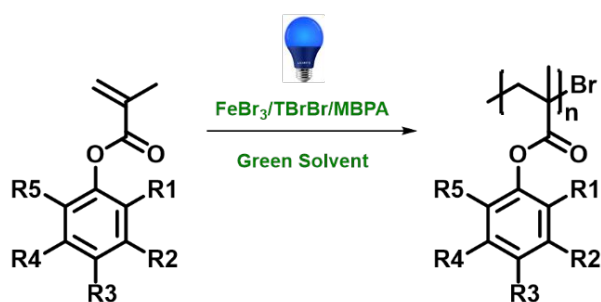
3.3 RAFT polymerization of PheMA

Into a 4 mL glass vial, 2-cyano-2-propyl benzodithioate raft agent (21.8 mg, 0.0986 mmol, 1 equiv.) was dissolved in 0.5 g of Tetraethylene Glycol Dimethyl Ether. PheMA (0.5 g, 3.0828 mmol, 50 equiv.), AIBN (1.01 mg, 0.0062 mmol, 0.1 equiv.), and a stirrer bar were added to the vial and it was sealed with a rubber septum. The reaction solution was deoxygenated by bubbling with nitrogen for 10 minutes. Polymerization was conducted in a pre-heated at 72°C oil bath, with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^1H NMR and SEC analysis.



Scheme S1: General schematic illustration for the synthesis of renewable monomers.

Figure S1: Home-made photo-reactor used for the photo-induced iron-catalyzed ATRP.



Scheme S2: General schematic illustration for the polymerization of the renewable monomers, utilizing photo-induced iron-catalyzed ATRP.

Table S1: ^1H NMR and SEC analysis for the synthesis of PPheMA in three different solvents, under otherwise identical conditions, utilising photo-induced iron-catalyzed ATRP.

[PheMA]:[MBPA]:[FeBr ₃]:[TBABr]	Solvent	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1:0.1	Tetraethylen glycol dimethyl ether	1.5	70	5900	5100	1.17
50:1:0.1:0.1	2-methyltetrahydrofuran	1.5	72	6100	5800	1.17
50:1:0.1:0.1	Cyclopentyl methyl ether	1.5	64	5400	5400	1.18

Table S2: ^1H NMR analysis showing the temporal control during the polymerization of PheMA, utilising photo-induced iron-catalyzed ATRP.

Entry	ON – OFF	Time (h)	Conversion (%)
1	ON	0-0.33	7
2	OFF	0.33-1.83	7
3	ON	1.83-2.16	21
4	OFF	2.16-4.16	23
5	ON	4.16-4.49	37
6	OFF	4.49-5.99	40
7	ON	5.99-6.99	70

Table S3: ^1H NMR and SEC analysis for the synthesis of PPheMA in tetraethylene glycol dimethyl ether, with targeted different degrees of polymerization, utilising photo-induced iron-catalyzed ATRP.

[PheMA]:[MBPA]:[FeBr ₃]:[TBABr]	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	D
25:1:0.1:0.1	1.5	64	2800	3400	1.15
50:1:0.1:0.1	1.5	70	5900	5100	1.17
67:1:0.1:0.1	1.5	62	7000	7400	1.18
133:1:0.3:0.3	1.5	60	13200	11000	1.22
266:1:0.8:0.8	1.5	50	21800	15100	1.27

Table S4: ^1H NMR and SEC analysis for the synthesis of PPheMA under non-deoxygenated condition in tetraethylene glycol dimethyl ether, utilizing photo-induced iron-catalyzed ATRP. The headspace or the reaction vessel was eliminated for this reaction.

[PheMA]:[MBPA]:[FeBr ₃]:[TBABr]	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	D
50:1:0.2:0.2	2	80	6700	5400	1.2

Figure S2: SEC analysis for the synthesis of PPheMA in tetraethylene glycol dimethyl ether, utilizing iron-catalyzed ATRP: a) in a 50 ul polymerization solution and b) in 100 ul of polymerization solution.

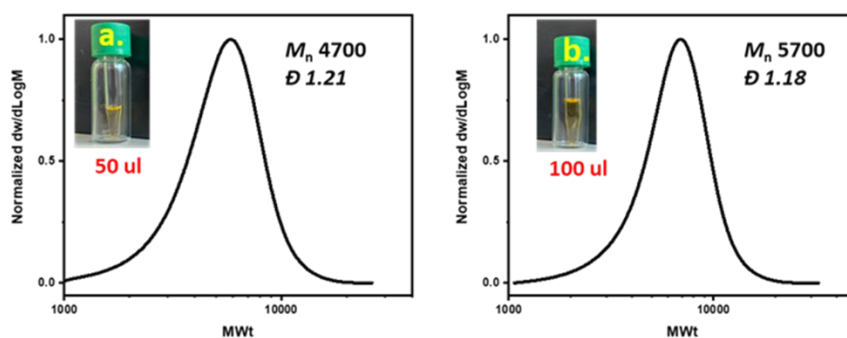


Table S5: ¹H NMR and SEC analysis for the synthesis of PPheMA macro initiator and its chain extension, after purification, with PheMA in tetraethylen glycol dimethyl ether, utilizing photo-induced iron-catalyzed ATRP.

[PheMA]:[MBPA]:[FeBr ₃]:[TBABr]	Block	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1:0.1	1	2	81	6800	6500	1.17
60:1:0.2:0.2	2	1.5	63	12900	12300	1.24

Table S6: ¹H NMR and SEC analysis for the synthesis of different renewable monomers, utilising photo-induced iron-catalyzed ATRP. For the polymerization of solid monomers (VaMA and SyrMA) 1:1.5 monomer-to-solvent(tetraethylen glycol dimethyl ether) ratio was used while for the rest liquid monomer the ratio was 1:1

[Monomer]:[MBPA]:[FeBr ₃]:[TBABr]	Monomer	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1:0.1	PheMA	2	81	6800	6600	1.17
50:1:0.1:0.1	CreMA	2	95	8600	6500	1.17
50:1:0.1:0.1	GuMA	2	91	9000	6400	1.17
50:1:0.1:0.1	ThyMA	2	58	6500	4400	1.16
50:1:0.1:0.1	VaMA	2	84	9500	11200	1.21
50:1:0.1:0.1	SyrMA	2	90	10200	7000	1.28

Table S7: ¹H NMR and SEC analysis for the synthesis of PGuMA macro initiator and its chain extension, after purification, with PheMA in tetraethylen glycol dimethyl ether using 10 an 20% of catalyst, utilizing photo-induced iron-catalyzed ATRP.

[Monomer]:[MBPA]:[FeBr ₃]:[TBABr]	Block	Monomers	Time (h)	Conversion (%)	M_n (Theo.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1:0.1	1	GuMA	2	91	9000	6500	1.17
100:1:0.1:0.1	2	PheMA	1.5	74	21000	17800	1.38
60:1:0.2:0.2	2	PheMA	1.5	70	15800	12600	1.24

Figure S3: SEC analysis for the synthesis of PGuMA macro initiator and its chain extension, after purification, with PheMA in tetraethylen glycol dimethyl ether, utilizing photo-induced iron-catalyzed ATRP: a) with 10% catalyst and b) 20% catalyst.

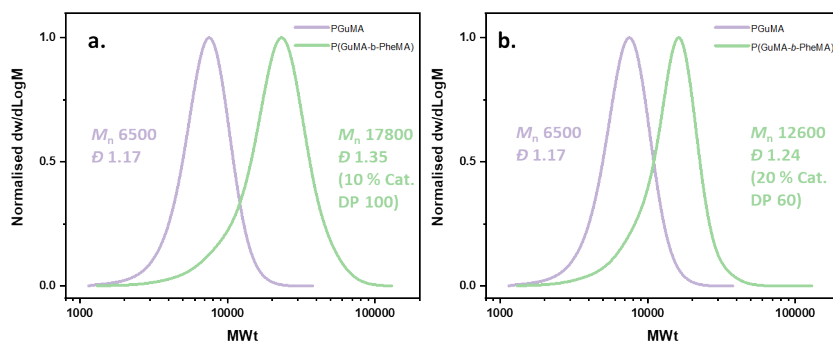


Table S8: ^1H NMR and SEC analysis for the polymerization kinetic experiment of PheMA in tetraethylen glycol dimethyl ether, utilizing RAFT polymerization.

[PheMA]:[RA]:[AIBN]	Time (h)	Conversion (%)	M_n (Theor.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1	0.5	12	1300	4000	1.30
50:1:0.1	2	60	5200	6500	1.37
50:1:0.1	3.5	81	6900	8300	1.37
50:1:0.1	7	93	7800	9500	1.43

Figure S4: SEC analysis for the synthesis of a) PSyrMA, b) PThyMA and c) PVaMA utilizing thermal RAFT polymerization

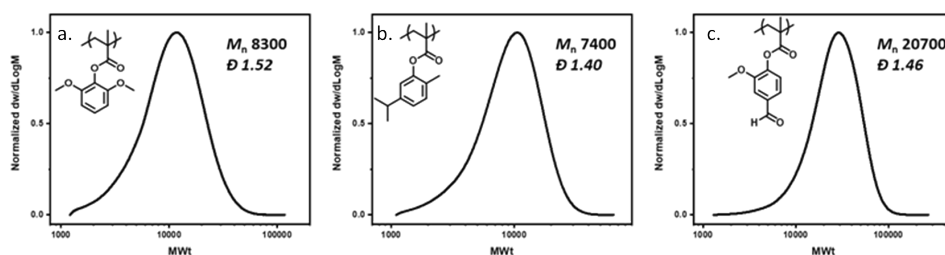


Figure S5: UV SEC analysis for the polymerization kinetic experiment of PheMA in tetraethylen glycol dimethyl ether, utilizing RAFT polymerization.

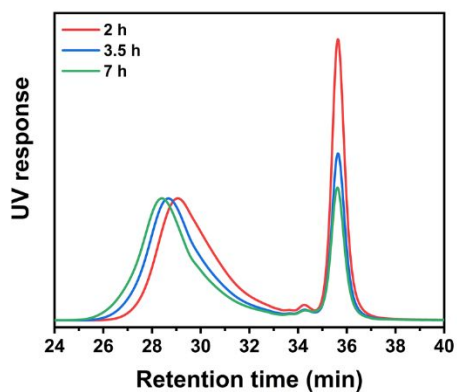


Table S9: ^1H NMR and SEC analysis for the polymerization kinetic experiment of PheMA in tetraethylen glycol dimethyl ether, utilizing photo-induced iron-catalyzed ATRP.

[PheMA]:[MBPA]:[FeBr ₃]:[TBABr]	Time (h)	Conversion (%)	M_n (Theor.) (Da)	M_n (SEC) (Da)	\bar{D}
50:1:0.1:0.1	0.5	14	1400	2500	1.16
50:1:0.1:0.1	2	62	5200	5200	1.18
50:1:0.1:0.1	3.5	82	6900	6200	1.18
50:1:0.1:0.1	7	96	8000	7200	1.20

Figure S6: SEC analysis for the polymerization experiment of PheMA in tetraethylen glycol dimethyl ether, utilizing PET-RAFT polymerization.

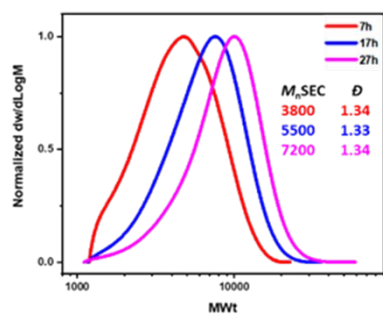


Figure S7: SEC analysis for the polymerization experiment of PheMA in tetraethylen glycol dimethyl ether, utilizing a) iron-catalyzed photo-induced ATRP at 70 °C and b) thermal RAFT polymerization at 70 °C .

