Supplementary Information

Controlled radical polymerization of vinyl ketones using visible light

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Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Radical inhibitors were removed from all monomers before use by running them through a basic aluminum oxide plug.

General analytical information

Nuclear magnetic resonance spectra were recorded on a Varian 600 MHz instrument. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent. Size exclusion chromatography (SEC) was performed at ambient temperature using chloroform with 0.25% triethylamine as the mobile phase in a Waters 2695 separation module with a Waters 2414 refractive index detector. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards. Dispersity (D) values are reported as the quotient of M_w/M_n .

General procedure for the polymerization of methyl vinyl ketone via PET-RAFT (MVK/CPDT = 100/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.010 g, 0.03 mmol) and Eosin Y (0.39 mg, 0.0006 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.24 ml). At this time, methyl vinyl ketone (MVK) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes). Under argon atmosphere, MVK (0.24 ml, 3 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 11 hours before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of the vinyl peaks of MVK ($\delta = 6.3$ -5.9 ppm) and the alkyl peaks of PMVK ($\delta = 3.0$ -1.0 ppm) in ¹H NMR spectrum, showing 92% conversion of MVK. The molecular weight ($M_n = 6.5$ kg/mol) and dispersity (D = 1.11) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The reaction crude mixture was diluted in chloroform and passed through basic alumina to remove Eosin Y. The organic layer was concentrated and precipitated into *n*-hexane ($M_n < 5$ kg/mol) or diethyl ether ($M_n > 5$ kg/mol) to give PMVK as a sticky, yellow solid.

Entry	MVK/CPDT	CPDT	MVK	Eosin Y DMSO		Irradiation
	(molar ratio)	(mmol)	(mmol)	(mmol)	(mL)	time (h)
1	50/1	0.060	3	0.0006	0.24	12
2	100/1	0.030	3	0.0006	0.24	11
3	200/1	0.015	3	0.0006	0.24	13
4	300/1	0.010	3	0.0006	0.004	13
5	500/1	0.006	3	0.0006	0.004	13
6	800/1	0.00375	3	0.0006	0.004	13

Reaction conditions with various MVK/CPDT ratio:

General procedure for the polymerization of methyl vinyl ketone in the absence of Eosin Y (MVK/CPDT = 100/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.010 g, 0.03 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.24 ml). At this time, methyl vinyl ketone (MVK) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes (Note: MVK is volatile). Under argon atmosphere, MVK (0.24 ml, 3 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 20 hours before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of the vinyl peaks of MVK ($\delta = 6.3-5.9$ ppm) and the alkyl peaks of PMVK ($\delta = 3.0-1.0$ ppm) in ¹H NMR spectrum, showing 90% conversion of MVK. The molecular weight ($M_n = 7.0$ kg/mol) and dispersity (D = 1.09) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The reaction crude mixture was diluted with chloroform and washed with brine three times to remove DMSO and dried with MgSO₄. The organic layer was concentrated and precipitated into diethyl ether to give PMVK as a sticky, yellow solid.

Representative procedure for the polymerization of methyl vinyl ketone via PET-RAFT without deoxygenation process (MVK/CPDT = 100/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.010 g, 0.03 mmol), Eosin Y (0.39 mg, 0.0006 mmol), and methyl vinyl ketone (MVK) (0.24 ml, 3 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.24 ml). The vial was then sealed and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 12 hours before turning off the light. The conversion of polymerization was calculated by comparing the integration values of the vinyl peaks of MVK (δ = 6.3-5.9 ppm) and the alkyl peaks of PMVK (δ = 3.0-1.0 ppm) in ¹H NMR spectrum, showing 86% conversion of MVK. The molecular weight (M_n = 8.9 kg/mol) and dispersity (D = 1.09) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The reaction crude mixture was diluted in chloroform and passed through basic alumina to remove Eosin Y. The organic layer was concentrated and precipitated into diethyl ether (M_n > 5 kg/mol) to give PMVK as a sticky, yellow solid.

Representative procedure for the polymerization of methyl vinyl ketone via PET-RAFT in the presence of triethylamine (MVK/CPDT = 100/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.010 g, 0.03 mmol) and Eosin Y (0.039 mg, 0.00006 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.24 ml). At this time, methyl vinyl ketone (MVK) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes (Note: MVK is volatile). Under argon atmosphere, MVK (0.24 ml, 3 mmol) and triethylamine (0.03 mmol, 4.2 μ l) were added to the vial containing other reagents. The vial was then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 4 hours before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of the vinyl peaks of MVK (δ = 6.3-5.9 ppm) and the alkyl peaks of PMVK (δ = 3.0-1.0 ppm) in ¹H NMR spectrum, showing 81% conversion of MVK. The molecular weight (M_n = 6.9 kg/mol) and

dispersity (θ = 1.10) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The reaction crude mixture was diluted in chloroform and passed through basic alumina to remove Eosin Y. The organic layer was washed with brine three times to remove DMSO and dried with MgSO₄. The organic layer was concentrated and precipitated into diethyl ether to give PMVK as a sticky, yellow solid.

Procedure for the polymerization of ethyl vinyl ketone via PET-RAFT (EVK/CPDT = 200/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.0052 g, 0.015 mmol) and Eosin Y (0.39 mg, 0.0006 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.24 ml). At this time, ethyl vinyl ketone (EVK) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes. Under argon atmosphere, EVK (0.30 ml, 3 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 12 hours before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of the vinyl peaks of EVK (δ = 6.4-5.8 ppm) and the alkyl peaks of PEVK (δ = 3.0-0.7 ppm) in ¹H NMR spectrum, showing 90% conversion of EVK. The molecular weight (M_n = 12.6 kg/mol) and dispersity (D = 1.14) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The reaction crude mixture was diluted in chloroform and passed through basic alumina to remove Eosin Y. The organic layer was concentrated and precipitated into *n*-hexane to give PEVK as a sticky, yellow solid.

Procedure for the polymerization of phenyl vinyl ketone via PET-RAFT (PhVK/CPDT = 200/1)

Added 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) (0.00346 g, 0.01 mmol), Eosin Y (0.26 mg, 0.0004 mmol), and phenyl vinyl ketone (PhVK) (0.264 g, 2 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.16 ml). The vial was then degassed by purging with argon for 10 minutes, then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue LEDs. The polymerization was left to stir for 12 hours before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of a vinyl peak of PhVK (δ = 6.5-6.4 ppm) and the aromatic peaks of PPhVK (δ = 8.1-6.7 ppm), showing 98% conversion of PhVK in ¹H NMR spectrum. The molecular weight (M_n = 17.7 kg/mol) and dispersity (D = 1.19) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The crude reaction mixture was precipitated into MeOH, redissolved in CHCl₃, concentrated under reduced pressure, and reprecipitated into MeOH (Note: Eosin Y and DMSO were removed by the precipitation into MeOH). The resulting polymer was obtained as a yellow solid.

Procedure for the block copolymerization of PMVK-b-PPhVK via PET-RAFT

Added PMVK-CTA ($M_n = 6.0 \text{ kg/mol}$ and $\mathcal{D} = 1.08$) (0.030 g, 0.005 mmol), Eosin Y (0.016 mg, 0.000025 mmol), and phenyl vinyl ketone (PhVK) (0.066 g, 0.5 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.2 ml). The vial was then degassed by purging with argon for 10 minutes, then sealed with Parafilm and irradiated on a stir plate in a glass dish lined with 465 nm blue

LEDs. The polymerization was left to stir for 90 minutes before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of a vinyl peak of PhVK (δ = 6.5-6.4 ppm) and the aromatic peaks of PPhVK (δ = 8.1-6.7 ppm) in ¹H NMR spectrum, showing 83% conversion of PhVK. The molecular weight (M_n = 14.3 kg/mol) and dispersity (D = 1.13) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The crude reaction mixture was precipitated into MeOH, redissolved in CHCl₃, concentrated under reduced pressure, and reprecipitated into MeOH. The resulting polymer was obtained as a yellow solid.

Procedure for the block copolymerization of PMVK-b-PMA via PET-RAFT

Added PMVK-CTA ($M_n = 6.0 \text{ kg/mol}$ and $\mathcal{D} = 1.08$) (0.060 g, 0.010 mmol) and Eosin Y (0.13 mg, 0.0002 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.4 ml). At this time, methyl acrylate (MA) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes. Under argon atmosphere, MA (0.091 ml, 1 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and placed on blue LED stir plate apparatus irradiating with 465 nm light. The polymerization was left to stir for 45 minutes before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of the methyl peak of MA ($\delta = 3.76 \text{ ppm}$) and the methyl ester peak of PMA ($\delta = 3.66 \text{ ppm}$) in ¹H NMR spectrum, showing 39% conversion of MA. The molecular weight ($M_n = 12.1 \text{ kg/mol}$) and dispersity ($\mathcal{D} = 1.10$) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The crude reaction mixture was diluted in chloroform, washed with brine three times, and dried with MgSO₄. The organic layer was concentrated under reduced pressure.

Procedure for the block copolymerization of PMVK-b-PDMA via PET-RAFT

Added PMVK-CTA ($M_n = 6.0$ kg/mol and D = 1.08) (0.060 g, 0.010 mmol) and Eosin Y (0.13 mg, 0.0002 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in DMSO (0.4 ml). At this time, N,N-dimethylacrylamide (DMA) was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes. Under argon atmosphere, DMA (0.10 ml, 1 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and placed on blue LED stir plate apparatus irradiating with 465 nm light. The polymerization was left to stir for 45 minutes before turning off the light and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of a vinyl peak of DMA ($\delta = 6.6-6.5$ ppm) and the N,N-dimethyl amide peaks of PDMA ($\delta = 3.25-2.75$ ppm) in ¹H NMR spectrum, showing 57% conversion of DMA. The molecular weight ($M_n = 13.4$ kg/mol) and dispersity (D = 1.11) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The crude reaction mixture was diluted in chloroform, washed with brine one time, and dried with MgSO₄. The organic layer was concentrated and precipitated into *n*-hexane. The precipitated into *n*-hexane.

Procedure for the block copolymerization of PMVK-b-PS via thermal RAFT¹⁹

Added PMVK-CTA ($M_n = 6.0$ kg/mol and D = 1.08) (0.060 g, 0.010 mmol) and azobisisobutyronitrile (AIBN) (0.4 mg, 0.002 mmol) to a 1-dram glass vial equipped with stir bar before dissolving in 2-butanone (0.12 ml). At this time, styrene was placed in another 1-dram glass vial. The vials were then degassed by purging with argon for 10 minutes. Under argon atmosphere, styrene (0.12 ml, 1 mmol) was taken and added to the vial containing other reagents. The vial was then sealed with Parafilm and stirred at 65 °C. The polymerization was left to stir for 6 hours before cooling down to 0 °C and opening the vial to air. The conversion of polymerization was calculated by comparing the integration values of a vinyl peak of styrene ($\delta = 5.2$ ppm) and the aromatic peaks of PS ($\delta = 7.7-6.2$ ppm) in ¹H NMR spectrum, showing 17% conversion of styrene. The molecular weight ($M_n = 9.4$ kg/mol) and dispersity (D = 1.09) of the polymer was obtained by SEC eluting with chloroform (using polystyrene standards). The polymer was purified by the following sequence: The crude reaction mixture was precipitated into MeOH, redissolved in CHCl₃, concentrated under reduced pressure, and reprecipitated into MeOH. The resulting polymer was obtained as a yellow solid.



Fig. S1 Representative ¹H NMR spectra of MVK monomer and crude PMVK reaction mixture.





Fig. S2 $CHCl_3$ SEC traces of PMVK monitored with time of light exposure.

Fig. S3 Plot of (a) $\ln([M]_0/[M]_t)$ and (b) M_n and D values vs time for polymerization of MVK using PET-RAFT with repeated "on-off" cycling of light.

Table S1 Polymerization of MVK in the absence of Eosin Y

$\begin{array}{c} \text{NC} \\ \text{Solvent, RT} \\ \text{CPTD} \end{array} \xrightarrow{\text{Blue LED (465 nm)}} \\ \text{Solvent, RT} \\ \text{NC} \\ \text{Solvent, RT} \\ \text{NC} \\ \text{Solvent, RT} \\ \text{NC} \\ \text{Solvent, RT} \\$									
Entry	M/I	Solvent	Air (O ₂)	TEA	Time	Conv. ^a	M , ^b	Ð ^b	
1	100	DMSO	-	-	20 h	90%	7.0k	1.09	
2	300	DMSO	-	-	12 h	80%	18.1k	1.16	
3	500	DMSO	-	-	12 h	84%	26.9k	1.26	
4	800	DMSO	-	-	11 h	68%	40.3k	1.31	
5	100	Bulk	-	-	12 h	75%	6.0k	1.10	
6	200	Bulk	-	-	12 h	13%	0.7k	1.09	
7	300	Bulk	-	-	11 h	17%	2.0k	1.35	
8	800	Bulk	-	-	20 h	21%	9.5k	1.17	
9	100	DMSO	-	Yes (1 eq.)	4 h	36%	4.3k	1.16	
10	100	.00 DMSO	Voc	Voc (2 og)	3 h	24%	2.4k	1.13	
			162	1 es (2 eq.) -	7 h	57%	5.0k	1.19	

^{*a*}Determined using ¹H NMR. ^{*b*}Measured by size exclusion chromatography (SEC) using CHCl₃ as an eluent and calibrated using polystyrene (PS) standards.



Fig. S4 Multi-gram synthesis of PMVK with no Eosin Y and no deoxygenation. (a) Reaction set-up depicting reaction vial surrounded by 465 nm blue LED strips with a jet stream of air to maintain ambient temperature. (b) 4.9 g of PMVK obtained after purification. (c) SEC-RI trace of PMVK.



Fig. S5 Overlay of SEC-UV (at 310 nm) and RI traces of PMVK ($M_n = 4.1 \text{ kg/mol}$ and D = 1.09)



Fig. S6 ¹H NMR spectrum and SEC-RI trace of PEVK



Fig. S7 ¹H NMR spectrum and SEC-RI trace of PPhVK



Fig. S8 ¹H NMR spectrum of PMVK-*b*-PPhVK



Fig. S9 ¹H NMR spectrum of PMVK-b-PMA



Fig. S10 ¹H NMR spectrum of PMVK-*b*-PDMA



Fig. S11 ¹H NMR spectrum and CHCl₃ SEC trace of PMVK-*b*-PS