Electronic Supplementary Information

Well-controlled Reversible Addition-Fragmentation Chain Transfer Radical Polymerisation under Ultraviolet Radiation at Ambient Temperature

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1) UV-vis spectroscopy for TPO, DDMAT and CDB

A 5.0 mmol L^{-1} TPO, DDMAT or CDB solution in methyl acrylate/benzene (3:1, v/v) was prepared at room temperature. The UV-vis spectra were recorded using a PerkinElmer lamda-25 UV/vis spectrometer at 25 °C. As shown in Figure S1, the results indicate strong absorption of CDB and TPO but weak absorption of DDMAT at λ = 365 nm; while, strong absorption of TPO but weak absorption of CDB and DDMAT at λ = 405 nm.

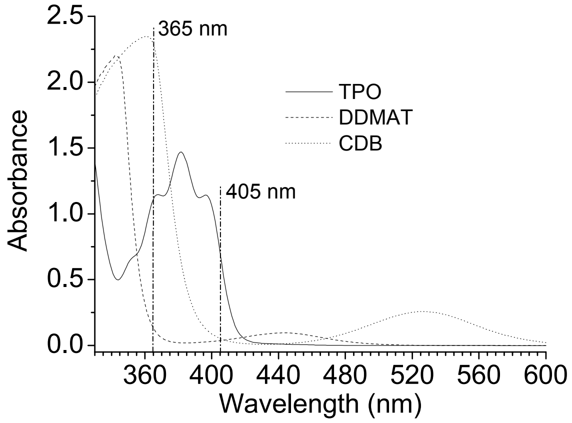

Figure S1 UV-vis spectra of 5.0 mmol L^{-1} TPO, DDMAT and CDB solutions in methyl acrylate/benzene (3:1, v/v) at 25 ºC.

2) Photolysis of CTAs (DDMAT and CDB)

Under full-wave UV radiation: A 5.2 mmol L^{-1} CTA (DDMAT or CDB) solution in methyl acrylate/benzene (3:1, v/v) was prepared at room temperature. Photolysis experiments of these CTAs were carried out in a 4 mL quartz cuvette (no absorption in the wavelength range of 254-405 nm) capped with rubber septa. The solution was deoxygenated by purging with argon for 15 min, followed by placing the quartz cuvette in a thermostatic water bath at 30 °C under full-wave UV radiation at intensity of 300 μW/cm^2. The UV intensity was measured using a radiometer with a 365 nm sensor. The UV-vis spectra of the resulting solutions were recorded at 25 °C using a PerkinElmer lamda-25 UV-vis spectrometer. The characteristic absorption of DDMAT at 443 nm or CDB at 525 nm was selected for determining the concentration of CTA.

Under long-wave UV radiation: A 5.2 mmol L^{-1} CTA solution in methyl acrylate/benzene (3:1, v/v) was prepared in a round-bottom flask. The solution was deoxygenated by purging with argon under stirring for 15 min. The flask was then placed in a thermostatic water bath at 30 °C under UV radiation at intensity of 300 μW/cm^2. Soda glass was placed between the flask and UV lamp to cut off the short-wave UV radiation below 313 nm [L. Fan, *Special Organic Synthesis techniques*, Press of Shanghai Jiaotong University, Shanghai, 1987, p9.]. The solutions (~3.0 mL) were taken out using degassed syringes at predetermined interval. The UV-vis spectra of the solutions were recorded at 25 °C.

As shown in Figure S2 and Figure 1, the photolysis of CTAs has been remarkably suppressed under long-wave UV radiation.

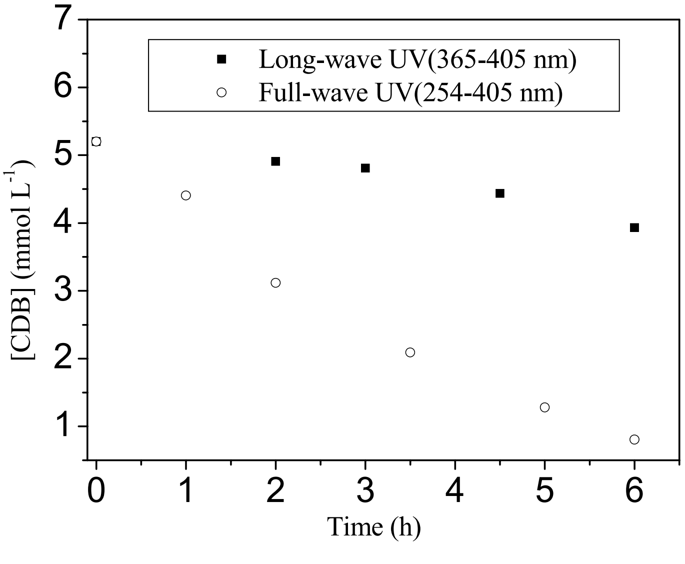

Figure S2 Photolysis of CDB under long-wave and full-wave UV radiation at intensity of 300 μW/cm^2 monitored by UV-vis spectrophotometry. $[CDB]_0$ = 5.2 mmol L^{-1} in methyl acrylate/benzene (3 : 1, v/v) at 30 °C.

3) RAFT polymerisation of MA under long-wave UV radiation at ambient temperature

The RAFT polymerisation protocol is as follows: Methyl acrylate (14.68 g, 170.7 mmol), DDMAT (0.40 g, 1.1 mmol), TPO (0.077 g, 0.22 mmol) and 5.0 ml benzene were charged into a 50 ml round-bottom flask. The solution was deoxygenated by purging with argon under stirring for 15 min. The flask was placed in a thermostatic water bath under UV radiation at intensity of 300 μW/cm^2 at 30 ^{o}C. Soda glass was placed between the flask and UV lamp to cut off the short-wave UV radiation below 313 nm. The solutions (~0.5 mL) were taken out at predetermined interval using a degassed syringe. The polymerisation was ceased by the addition of hydroquinone inhibitor. The conversion was determined by ^{1}H NMR using a 400 MHz Bruker AV-400 spectrometer. The conversions of polymerisation were calculated according the following equation:

$$\text{Conversion} = (\boldsymbol{I}_{3.5\text{-}3.8} - \boldsymbol{I}_{5.8\text{-}6.4}) / \boldsymbol{I}_{3.5\text{-}3.8}$$

Where, $\boldsymbol{I}_{3.5\text{-}3.8}$ is the integral of the resonance at δ = 3.5-3.8 ppm ($\text{C}\underline{\mathbf{H}}_3\text{OCO}$ of both PMA and MA monomer), $\boldsymbol{I}_{5.8\text{-}6.4}$ is the integral of the resonance at δ = 5.8-6.4 ppm ($\text{C}\underline{\mathbf{H}}_2\text{=C}\underline{\mathbf{H}}\text{COO}$ of MA monomer). The residual monomer and benzene was removed by rotary evaporation, the resulting polymer was dried in a vacuum oven at 30 ^{o}C. The molecular weights and polydispersities were determined using a Waters GPC. THF was used as an eluent at 25 ^{o}C.

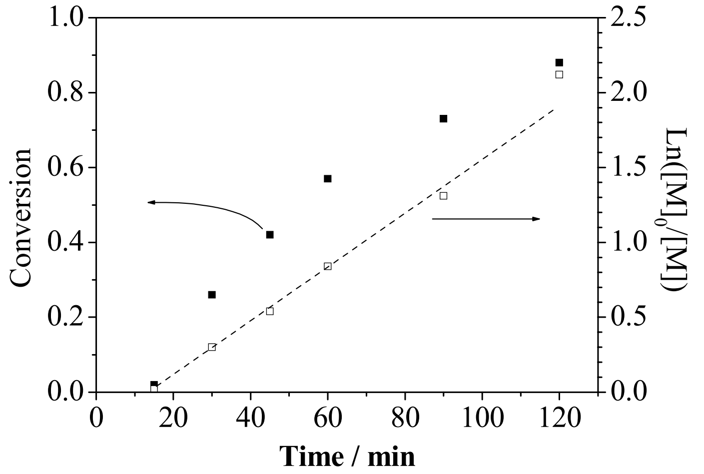

Figure S3 Typical pseudo first order kinetics with respect to MA monomer for the polymerisation of MA under long-wave UV radiation. Conditions: I = 300 μW/cm^2, $[\text{MA}]_0$= 8.1 mol L^{-1}, in benzene using DDMAT as a CTA and TPO as a photo-initiator at 30 ^{o}C.

^{1}H NMR studies indicate that this polymerisation is a typical pseudo first order kinetics (see Figure S3).

4) Self-block chain extension experiment

Synthesis of PMA-based macro-CTA: The synthesis protocol is the same as the RAFT polymerisation of MA mentioned above except $[\mathrm{DDMAT}]_0$: $[\mathrm{TPO}]_0$ is 10 : 1 rather than 5:1, the intensity of long-wave UV radiation is 100 μW/cm^2 rather than 300 μW/cm^2. The polymerisation was ceased after reaction for 345 min. The resulting polymer was isolated by precipitation from a large excess of petroleum ether: conversion = 84 % (^{1}H NMR results); M_n = 10 100, M_w/M_n = 1.06 (GPC results).

RAFT polymerisation of MA using a PMA-based macro-CTA: The self-block chain extension protocol is the same as above-mentioned except $[\mathrm{MA}]_0$ = 5.75 mmol L^{-1}, $[\mathrm{MA}]_0$: [macro-CTA]$_0$: $[\mathrm{TPO}]_0$ = 267 : 1 : 0.2, the long-wave UV radiation with intensity of 100 μW/cm^2. The polymerisation was ceased after reaction for 120 min.: conversion = 46 % (gravimetrical results), M_n = 21 000, M_w/M_n = 1.17 (GPC results).