Supporting Information

Well-defined amine-reactive polymethacrylates through organocatalyzed controlled radical polymerization

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Materials

All reagents used in this study were purchased from Sigma-Aldrich, unless otherwise noted. Acetone (99.9%), benzylamine (98%, Alfa Aesar), dichloromethane (DCM, 99.5%), diethyl ether (99%), methanol (CH_3OH), methyl methacrylate (MMA, 99%), neutral aluminum oxide (Roth), poly(ethylene glycol) methyl ether methacrylate (mPEGMA, M_n= 475 g.mol^{-1}), sodium iodide (NaI, >99%), tetrabutylammonium iodide (TBAI, >98%, TCI), tetrahydrofuran (THF, 99.9%), and tri(n-butyl)amine were used as received. MMA and mPEGMA monomers were stored in the presence of molecular sieves (3Å) for at least 1 week before use and passed through a short column of neutral aluminum oxide before polymerization. 2-(1-bromoethyl)-4,4-dimethyloxazol-5(4H)-one (bromo-azlactone) was synthesized according a literature procedure.[1] The UV nail box (Mylee, 36 W, 365 nm) equipped with four 9W bulbs and computer fans were purchased from Amazon.

Characterization

High resolution mass spectrometry (HRMS): Experiments were performed with a Synapt G2 HDMS quadrupole/time-of-flight (Manchester, UK). Samples were introduced at a 10 µl min^{-1} flow rate (capillary voltage +2.8kV, sampling cone voltage: varied between +20V and +60V) under a desolvation gas (N_2) flow of 100 L h^{-1} heated at 35°C. Accurate mass experiments were performed using reference ions from PPG, PEG or CH_3COONa internal standard. All the samples were dissolved in methanol doped with 3mM ammonium acetate prior to analysis. Data analyses were conducted using MassLynx 4.1 programs provided by Waters.

[1] H. T. Ho, F. Leroux, S. Pascual, V. Montembault and L. Fontaine, *Macromol. Rapid Commun.*, 2012, **33**, 1753–1758.

Fourier-Transformation Infrared (FT-IR): Spectra were recorded using a Perkin Elmer Spectrum Two FT-IR Spectrometer with an ATR accessory.

Nuclear magnetic resonance (NMR): Spectroscopies were recorded by using Bruker AC 300 and 400 MHz.

Size exclusion chromatography (SEC): Molar mass ($M_{n,SEC}$) and polydispersity ($Đ$) of poly(methyl methacrylate) in the kinetic polymerization studies of MMA were determined by size exclusion chromatography (SEC) using the EcoSEC apparatus from PSS. Otherwise, the polymers were analyzed with SEC apparatus from Agilent Technologies. For both systems, $M_{n,SEC}$ and $Đ$ were calculated by means of poly(methyl methacrylate) (PMMA) calibration curve using PMMA standards from 1.86 to 520.0 Kg.mol^{-1}(Agilent, USA).

EcoSEC system: The apparatus was equipped with a dual flow cell refractive index detector. The eluent was THF at a flow rate of 0.3 mL.min^{-1} for the sample pump and 0.15 mL.min^{-1} for the reference pump. The stationary phase was a combination of one PL Resipore (50x4.6) mm guard column and two PL Resipore (250x4.6) mm columns thermostated at 40°C. Samples were prepared at concentration of 0.25 wt.% in THF containing 0.25 vol.% of toluene, as a flowmarker. Injection volume was 20 μL.

SEC from Agilent Technologies: The apparatus was equipped with a 1260 infinity pump (Agilent Technologies), a 1260 infinity autosampler (Agilent Technologies), a 1260 infinity UV photodiode array detector (Agilent Technologies), a 1260 infinity RI detector (Agilent Technologies). The stationary phase was composed of 2 PSS-SDV Linear M column and a precolumn at 40°C. Mobile phase was THF at 1 mL.min^{-1}. Samples were solubilized in a mixture of THF and toluene (0.25wt %) and filtered through 0.45 μm PTFE syringe filter (Agilent). Samples concentration was about 2.5 mg/mL.
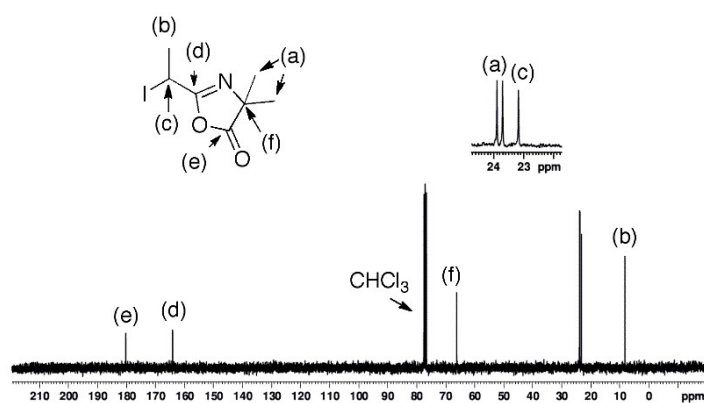
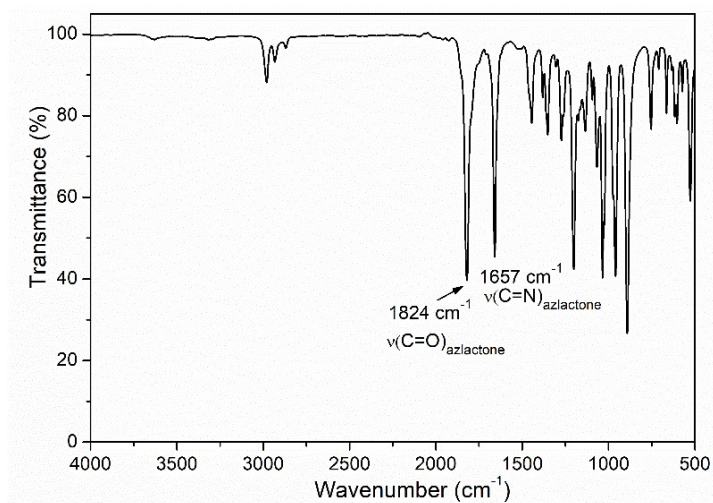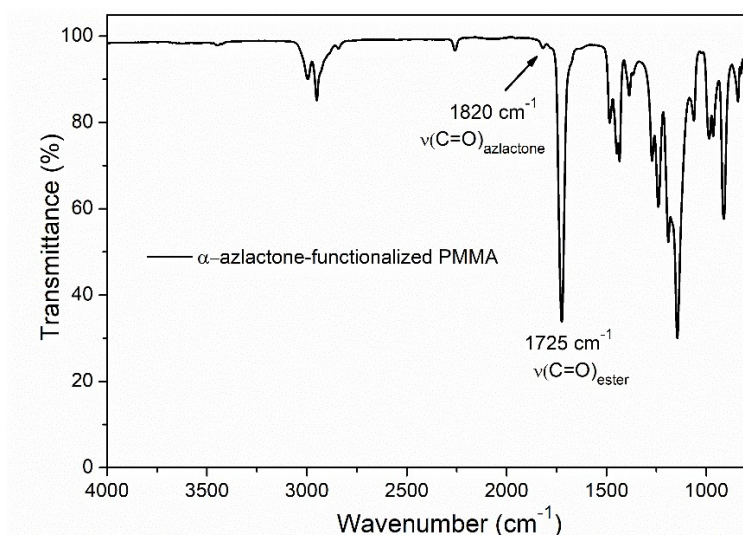**Fig. S2**: FT-IR spectrum of I-Azl.

Fig. S3: FT-IR spectrum of α-azlactone-functionalized PMMA with $M_{n,SEC}$ = 9460 g.mol^{-1} and $Đ$ = 1.19.

Table S1: Photo-RCMP of mPEGMA (λ= 365 nm) using tri(n-butylamine) as the catalyst and I-Azl as the initiator with an initial molar ratio [mPEGMA]$_0$:[I-Azl]$_0$:[tri(n-butyl)amine]$_0$ = 40:1:0.95

Run	Time (min)	Conv.[a] (%)	$M_{n,th}$[b] (g.mol^{-1})	$M_{n,SEC}$[c] (g.mol^{-1})	$Đ$[c]
1	0	0	267	-	-
2	20	0	267	-	-
3	40	4	1027	-	-
4	60	10	2167	8500	1.12
5	90	17	3497	10800	1.13
6	120	29	5777	13220	1.13
7	180	44	8627	15650	1.18
8	240	56	10907	18410	1.18

[a] Determined by ^{1}H NMR spectroscopy. [b] $M_{n,th}$ = M_{I-Azl} + ($40*$Conv.$*M_{mPEGMA}$/100) with M_{mPEGMA}= 475 g.mol^{-1}. [c] Determined by SEC with THF as an eluent and standard PMMA for the calibration curve.

Table S2: Photopolymerization of mPEGMA (λ = 365 nm) using TBAI as the catalyst and I-Azl as the initiator with an initial molar ratio of [mPEGMA]$_0$:[I-Azl]$_0$:[TBAI]$_0$ = 34:1:0.41

Run	Time (min)	Conv.[a] (%)	$M_{n,th}$[b] (g.mol^{-1})	$M_{n,SEC}$[c] (g.mol^{-1})	$Đ$[c]
1	0	0	267	-	-
2	60	5	1075	6460	1.12
3	120	15	2690	8890	1.14
4	180	25	4305	10860	1.15
5	240	35	5920	12060	1.17
6	300	43	7212	13560	1.17
7	360	49	8181	15540	1.19

[a]Determined by ^{1}H NMR spectroscopy. [b]$M_{n,th}$ = M_{I-Azl} + ($34*$Conv.$*M_{mPEGMA}$/100) with M_{mPEGMA}= 475 g.mol^{-1}. [c]Determined by SEC with THF as an eluent and standard PMMA for the calibration curve.

Table S3: Synthesis of azlactone-functionalized polymers for coupling with benzylamine

Entry	monomer	[monomer]$_0$: [I-Azl]$_0$: [catalyst]$_0$	Time (min)	Conv.[a] (%)	$M_{n,SEC}$[b] (g.mol^{-1})	$Đ$[b]
1	MMA	120:1:1.21[c]	60	53	9180	1.22
2	mPEGMA	50:1:0.95[d]	150	65	20770	1.20

[a] Determined by ^{1}H NMR spectroscopy. [b] determined by SEC using THF as an eluent and standard PMMA for the calibration curve. [c] using TBAI as the catalyst and a temperature of 80°C. [d] using photo-RCMP with tri(n-butyl)amine as the catalyst.
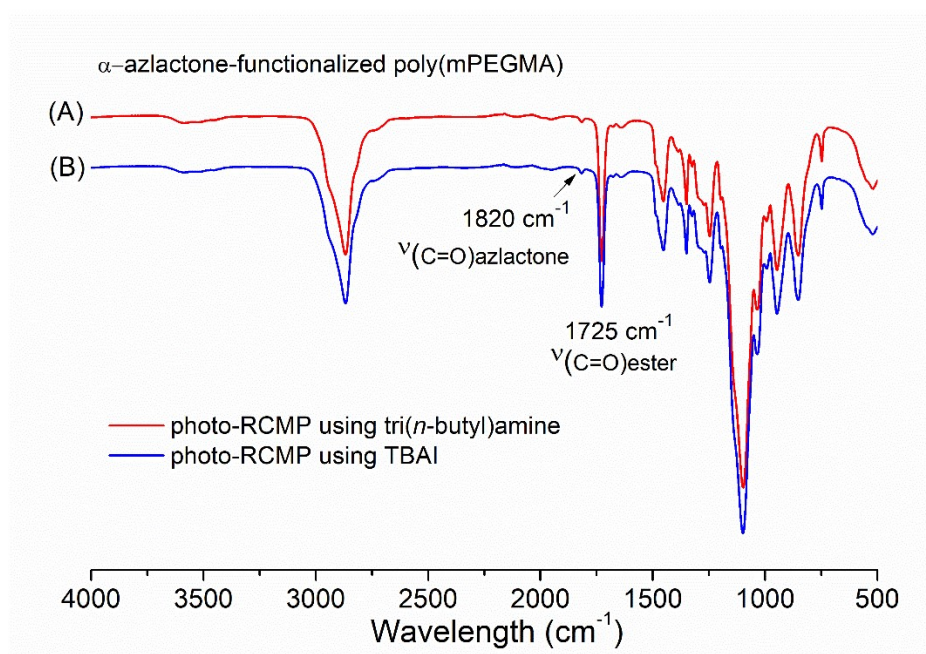

Fig. S4: FT-IR spectra of α-azlactone-functionalized poly(mPEGMA) synthesized by RCMP photo-polymerization conditions with (A) using tri(n-butylamine) and (B) using TBAI catalysts.
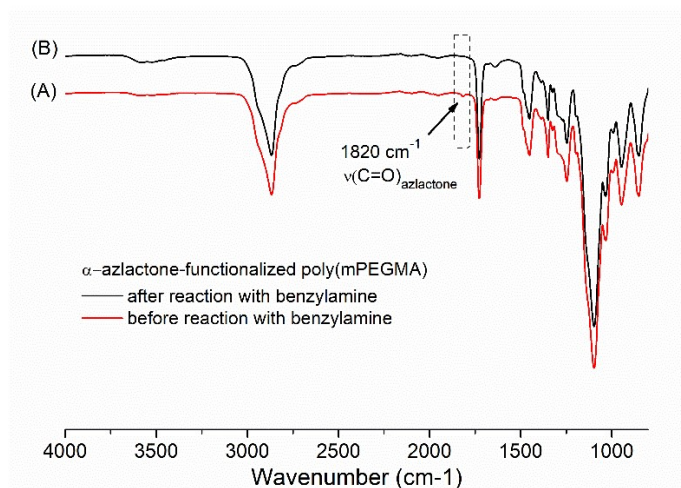
Fig. S5: FT-IR spectra of α-azlactone-functionalized poly(mPEGMA) ($M_{n,SEC}$ = 20770 g.mol^{-1} and $Đ$ = 1.20) (A) before and (B) after reaction with benzylamine.
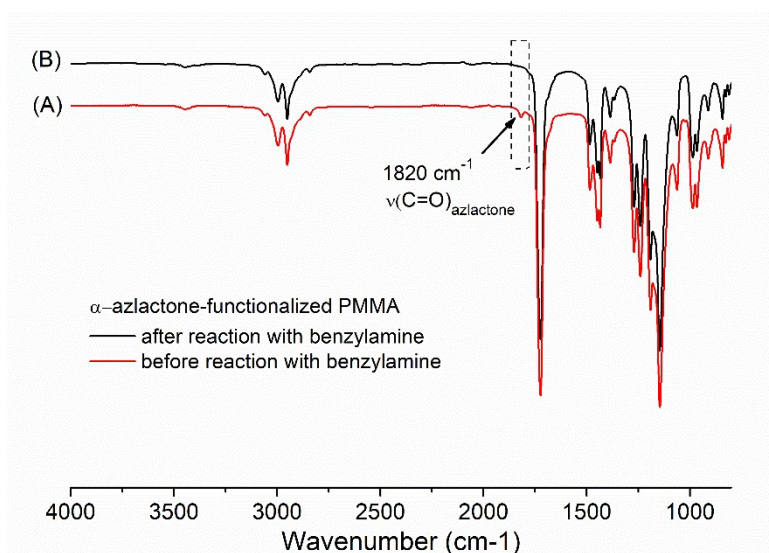

Fig. S6: FT-IR spectra of α-azlactone-functionalized PMMA ($M_{n,SEC}$ = 9180 g.mol^{-1} and $Đ$ = 1.22) before (A) and after (B) reaction with benzylamine.