Electronic Supporting Information

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High Fidelity Vinyl Terminated Polymers By Combining RAFT and Cobalt Catalytic Chain Transfer (CCT) Polymerization Methods

Alexander H. Soeriyadi,[a] Cyrille Boyer,[a]* James Burns,[b] C. Remzi Becer,[b] Michael R.Whittaker,[a] David M.Haddleton,[b] Thomas P. Davis[a]*

[a]*Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering,*

The University of New South Wales, Sydney, NSW 2052, Australia.

[b]*Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom.*

Correspondence to: T.P. Davis (t.davis@unsw.edu.au) & C. Boyer (cboyer@unsw.edu.au)

Experimental Part:

Materials

Methyl methacrylate (MMA, 99%, Sigma-Aldrich) and *n*-butyl methacrylate (BMA, 99%, Sigma-Aldrich) were de-inhibited by passing through a column of activated basic alumina. De-inhibited monomers were stored at -18 °C. The initiator 2, 2'-azobisisobutyronitrile (AIBN) was re-crystallized twice from methanol. High purity N_2 (Linde gases) was used for reaction solution purging. RAFT agent 2-(2-cyanopropyl)-dithiobenzoate (CPDB) was synthesized according to a previously reported method.[1]

Synthesis of Reagents

Dithiobenzoyl disulfide, 2-(2-*cyanopropyl)dithiobenzoate (CPDB)* (**RAFT 1**) and 4-cyanopentanoic acid dithiobenzoate (CADB) (**RAFT 2**) were prepared according to the litterature.[1]

COBF was prepared according to Bakac *et al.*[2]

Polymerization of Methyl Methacrylate and n-Butyl Methacrylate

Polymerization of methyl methacrylate was carried out in bulk employing AIBN as an initiator and CPDB 2(2-cyanopropyl)dithiobenzoate (CPDB) as a RAFT agent. Typically, AIBN (0.01 g, 6.09×10^{-5} mol) and CPDB (0.23 g, 1.0×10^{-3} mol) were prepared. Methyl methacrylate (1.18 g, 1.2×10^{-2} mol) in acetonitrile (1 mL) was then mixed with the AIBN and CPDB. The mixture was then thoroughly deoxygenated by purging with nitrogen gas for 20 minutes, and then, placed in oil bath at 80 °C. A sample was taken after 90 mins of polymerization to allow GPC and NMR analysis (conversion ~ 70-80%). At a designated time, deoxygenated stock solution of COBF (2 ml, 2.5 mg/ml) was transferred via a cannula to the polymerization mixture. The reaction was performed at 80 °C for 14 hours. At the end of the reaction, the polymer was isolated by precipitation in cold petroleum ether, before analyses by NMR, GPC, and ESI-MS.

COBF stock solution was prepared by dissolving COBF catalyst (25.0 mg) in deoxygenated acetonitrile (10 mL). The solution was purged with N_2 gas for at least 1 hour to remove oxygen.

A similar procedure was used for all polymers, i.e. PMMA and PBMA.

Copolymerization of macromonomers with ethyl acrylate

Copolymerizations of both PMMA and P*n*BMA macromonomers with ethyl acrylate were performed as follows: A solution of macromonomer, ethyl acrylate, AIBN, and toluene was prepared, nitrogen purged, and then heated at 60°C in an oil bath overnight. The resulting copolymers were recovered by precipitation in cold methanol (0°C) before drying in vacuo overnight. A typical copolymerization was as followed: PMMA macromonomer (0.03 g, 3.0×10^{-5} mol), ethyl acrylate (0.3 g, 3.0×10^{-3} mol), AIBN (0.012 g, 7.3×10^{-4} mol), and Toluene (5 ml) were mixed in round bottom flask. The resulting copolymer was characterized by SEC and NMR.

Analyses

Gel permeation chromatography (GPC) measurements. THF GPC was performed on a Shimadzu modular system, comprised of an auto-injector and a Polymer Laboratories 5.0 µm bead size guard column (50*7.5 mm), followed by three linear PL column and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL.min^{-1}. The GPC System was calibrated using linear polystyrene standards. DMAc GPC analyses of the polymers were performed in *N,N*-dimethylacetamide [DMAc; 0.03% w/v LiBr, 0.05% 2, 6–di-Butyl-4-methylphenol (BHT)] at 50 °C (flow rate = 1 mL.min^{-1}) using a Shimadzu modular system comprised of an SIL-10AD auto-injector, a PL 5.0-mm bead-size guard column (50 × 7.8 mm) followed by four linear PL (Styragel) columns (10^5, 10^4, 10^3, and 500Å) and an RID-10A differential refractive-index detector. Calibration was achieved with commercial polystyrene standards ranging from 500 to 10^6 g/mol.

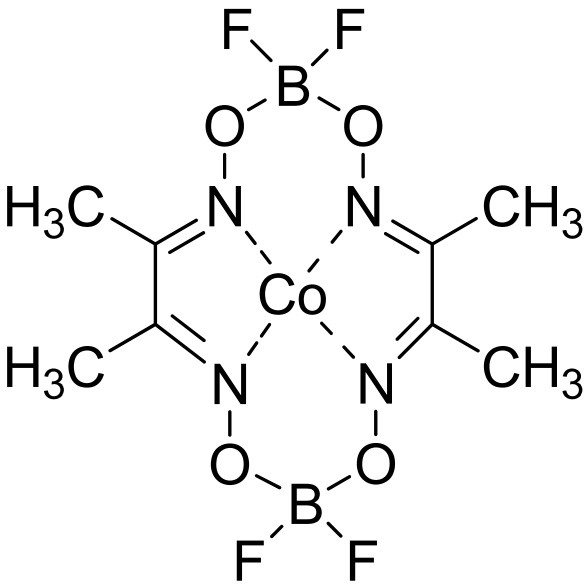
Nuclear Magnetic Resonance (NMR). Structures of the synthesized compounds were analyzed by ^{1}H NMR spectroscopy using a Brucker DPX 300 spectrometer at 300 MHz for hydrogen nuclei and 75 MHz for carbon nuclei.

UV-visible spectroscopy. UV-visible spectra were recorded using a CARY 300 spectrophotometer (Bruker) equipped with a temperature controller.

Electrospray Ionization Mass Spectrometry (ESI-MS).All samples were analyzed using a Thermo Finnigan LCQ Deca quadrupole ion trap mass spectrometer (Thermo Finnigan, San Jose, CA), equipped with an atmospheric pressure ionization source operating in the nebulizer assited electrospray mode and was used in positive ion mode. Mass calibration was performed using caffeine, MRFA, and Ultramark 1621 (Aldrich) in the *m/z* range of 195-1822 Da. All spectra was acquired within the *m/z* range of 150 – 2000 Da, and typical instrumental parameters were a spray voltage of 4.5 kV, a capillary voltage of 44 V, a capillary temperature of 275 °C and flow rate of 5 μL/min. Nitrogen was used as sheath gas (flow: 50% maximum) and helium was used as auxiliary gas (flow: 5% maximum). 30 microscans, with maximum inject time of 10ms per microscan. For each respective scan, approximately 35 scans were averaged to obtain the final spectrum. The solvent used was a 3:1 mixture of DCM: methanol with a sodium acetate concentration of 0.3 μM. Sodium acetate was added to the solvent prior to analyses to ensure ionization and to suppress Potassium salt peaks. All theoretical molecular weights were calculated using the exact mass for the first peak in any given isotopic pattern. The molecular weights of the most abundant isotopes were calculated using the following values: C^{12} = 12.000000; H^1 = 1.007825; O^{16} = 15.994915; Na^{23} = 22.989768.

Matrix Assisted Laser Desorption Ionization Time-of-flight Mass Spectrometry (MALDI): MALDI mass spectra were recorded on an Applied Biosystems Voyager DE STR MALDI-TOF spectrometer Applied Biosystems, the Netherlands) equipped with 2 m linear and 3 m reflecting light paths and a 337 nm nitrogen laser (3 ns pulse). All mass spectra were obtained with an accelerating potential of 20kV in positive ion mode and in reflector mode. Typically, the data obtained from 200 shots were signal averaged for final spectrum. The matrix used was 2,5-Dihydrobenzoic acid (DHB) (20mg/ml) and sample were dissolved in DCM (1 mg/ml). Analyte solutions were prepared by mixing 10 μL of the matrix solution and 10 μL of the sample and were then spotted on the sample plate and dried at room temperature

Supplementary Figures:



Scheme S1. Chemical structure of CoBF.

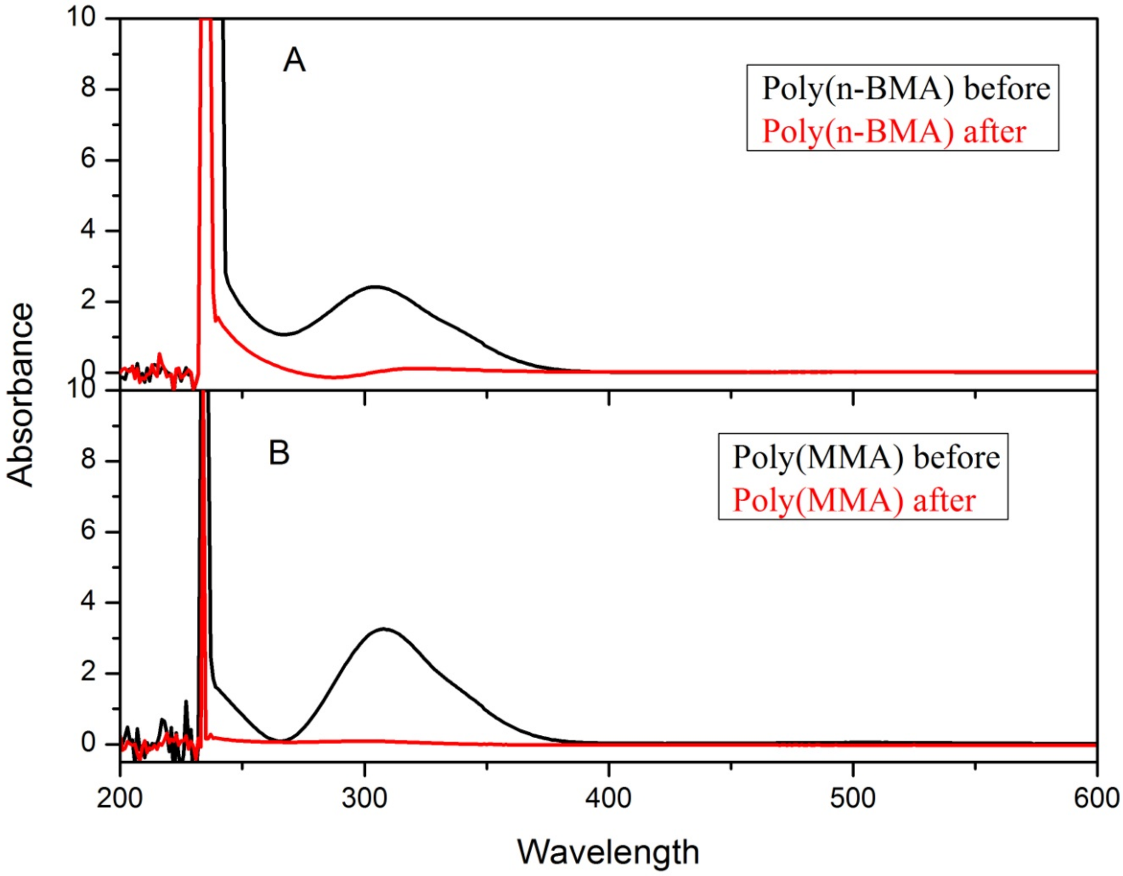


Figure S1. UV-visible spectra of (A) PBMA ($M_{n,\ GPC}$ = 18 850 g/mol, run #6 of **Table S1**) and (B) PMMA (M_n = 5 700 g/mol, run # 4 of **Table S1**) before and after reaction with CoBF.

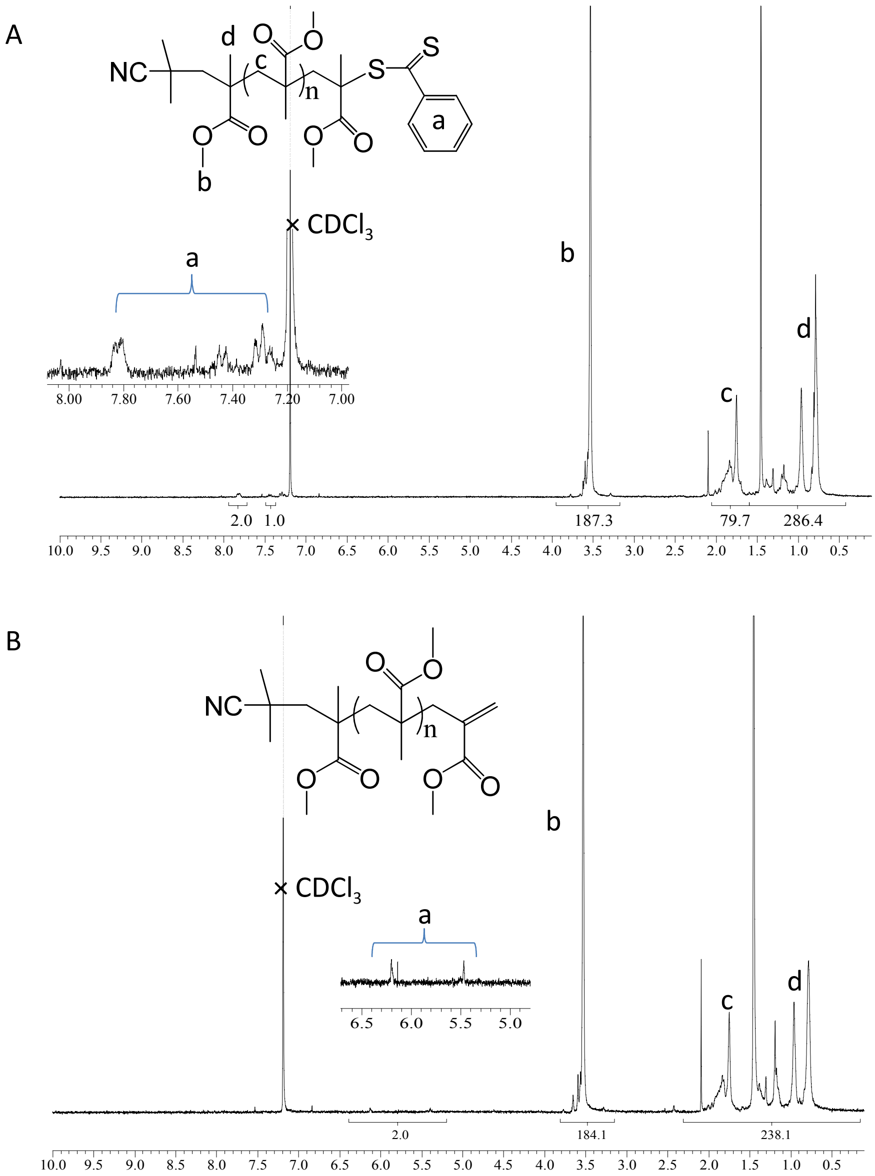


Figure S2. ^{1}H NMR spectra of PMMA: A- terminated by RAFT agent (before addition of COBF) ($M_{\text{n, NMR}}$ = 6 300 g/mol), and B- after reaction with CoBF ($M_{\text{n, NMR}}$ = 6 150 g/mol), recorded in $CDCl_3$, purified by several precipitations (at least 5 times) in petroleum ether.

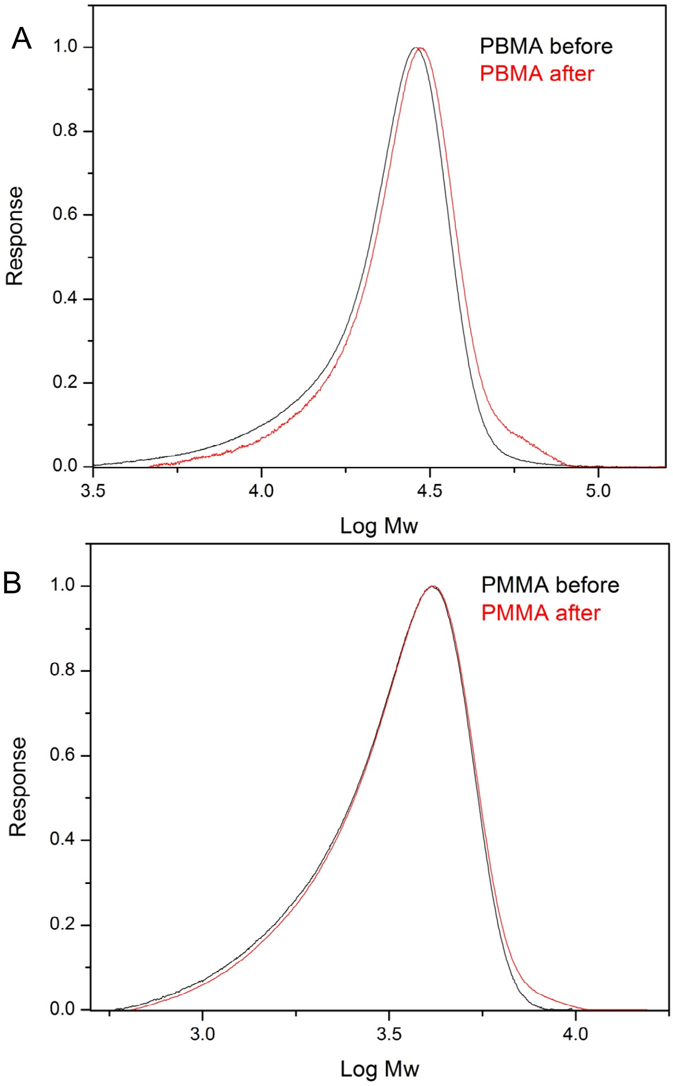


Figure S3. GPC traces of (A) PBMA (run # 6 in **Table S1**) and (B) PMMA (run # 5 in **Table S1**) before and after addition of COBF with refractive index detector.

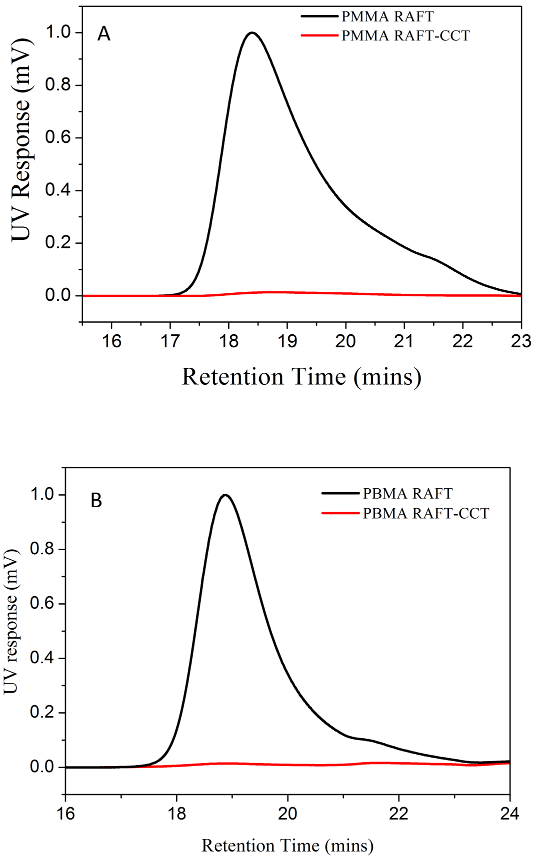


Figure S4. GPC traces of PMMA (run # 4 in **Table S1**) and PBMA (run # 6 in **Table S1**) before and after addition of COBF using UV detector. Concentration 1 mg/mL, elution solvent DMF.

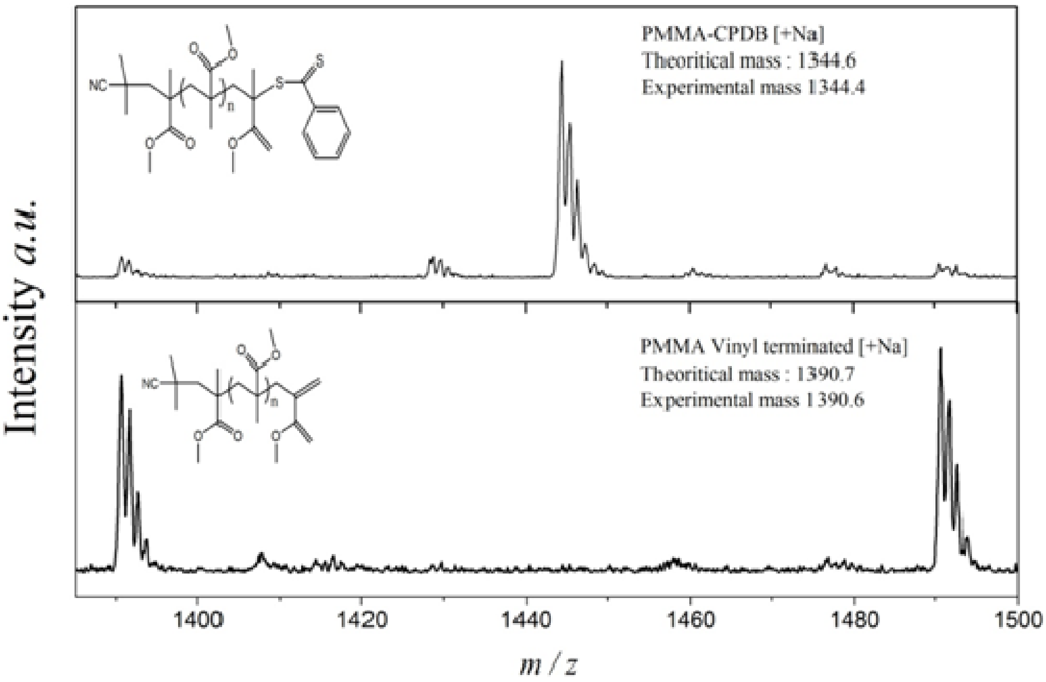


Figure S5. ESI-MS spectra PMMA ($M_{n,\,GPC}$ = 3 190 g/mol, run # 2 of **Table S1**) before (above) and after (below) addition of COBF. The peak assignments are reported in **Table S2**.

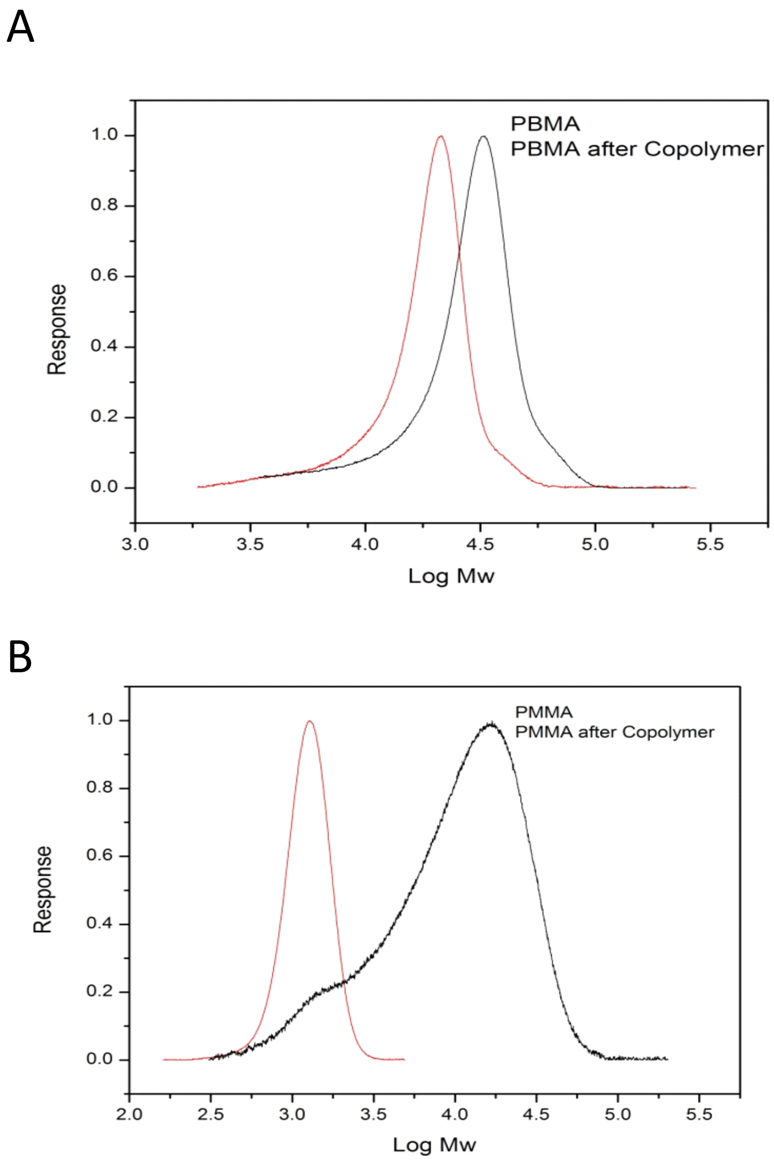


Figure S6. GPC traces (A) - of PBMA and (B)- of PMMA before copolymerization (red) and after copolymerization (black).

Note: the concentration in macromonomer (before and after copolymerization) is conserved constant to allow a comparison.

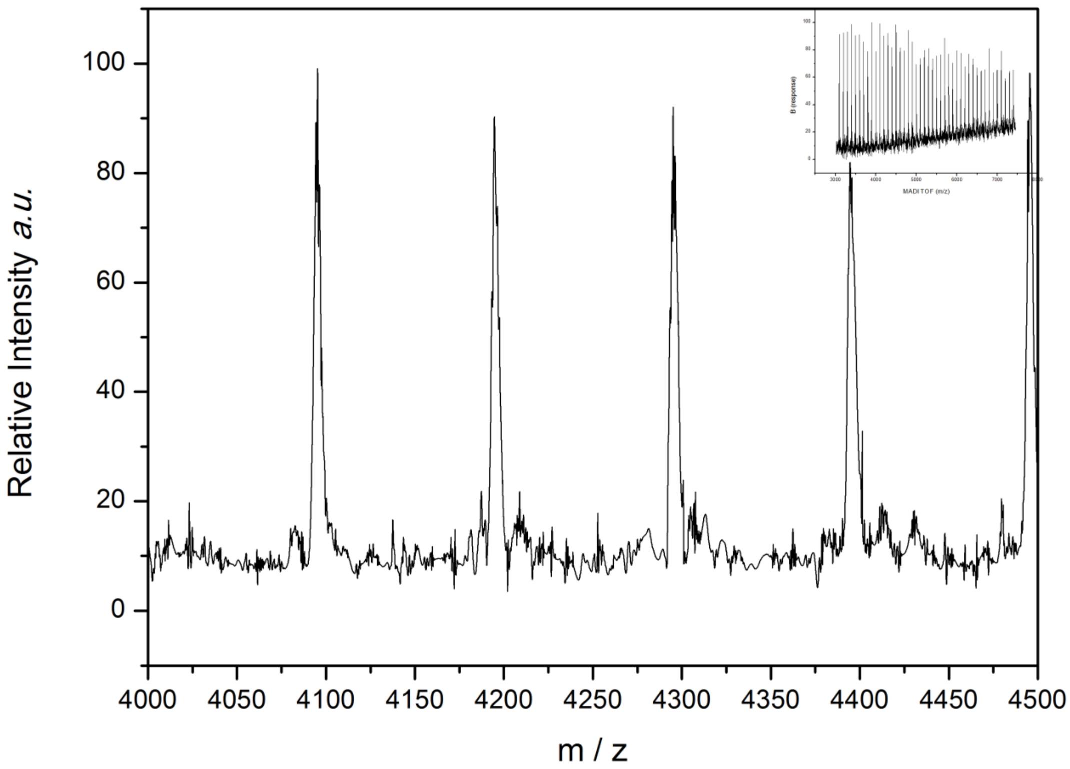


Figure S7. Mass Spectrum of PMMA RAFT-CCT (run # 4 table S1) obtained via MALDI-TOF showing single polymer population with mass in perfect agreement with vinyl terminated PMMA (experimental value = 4194.8 (theoretical value = 4194.6))

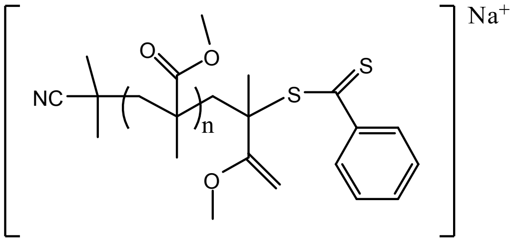
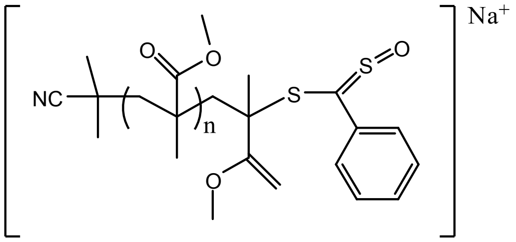
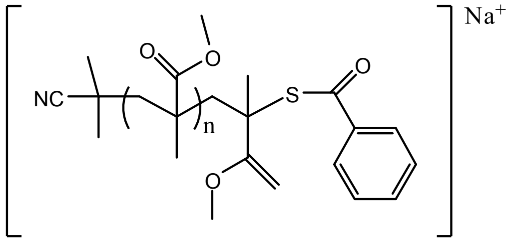
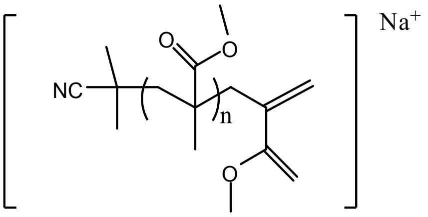
Table S1. Recapitulative of polymers used in this study.

Runs	Polymers	Before addition			After addition			*functionality*[c]
		M_n[a] (g/mol)	PDI[a]	M_n[b] (g/mol)	M_n[a] (g/mol)	PDI[a]	M_n[b] (g/mol)	(%)
1	PMMA[d]	1100	1.08	-	1000	1.08	-	100
2	PMMA[d]	3190	1.17	2800	3089	1.18	2900	100
3	PMMA[e]	4300	1.12	4200	4200	1.12	4050	100
4	PMMA[d]	5700	1.16	6300	5550	1.20	6150	> 95
5	PMMA[e]	6200	1.13	7500	6000	1.12	7200	100
6	PBMA[d]	18 850	1.26	22 400	21 934	1.21	23 500*	> 95

Note: a- determined by GPC (using poly(styrene calibration), b- calculated by ^{1}H NMR using Z group of RAFT agent as reference and vinylic bond as reference for RAFT polymer and macromonomer, respectively; c- functionality is calculated using the ratio of vinylic signal over the R groups of RAFT agent (functionality = $\int(a/2)/(e/4)$) for CADB used as RAFT agent (2); d- and e- polymers synthesized using **1** or **2** as RAFT agents.

*The slight increase of molecular weight (difference 5%) is due to the purification process, i.e. precipitation of PBMA in methanol removing short molecular weight.

Table S2. Peak assigned for ESI-MS mass spectra in **Figure S5**. All mass indicated good agreement with theoretical value with error within the error of the instrument of ± 0.3 Da.

Compound	m/z experimental	m/z theoretical	m/z error
	1344.4	1344.6	0.2
	1360.4	1360.6	0.2
	1328.5	1328.6	0.1
	1390.6	1390.7	0.1

REFERENCES:

1. Y. Mitsukami, M. S. Donovan, A. B. Lowe and C. L. McCormick, *Macromolecules*, 2001, **34**, 2248-2256.
2. A. Bakac, M. E. Brynildson and J. H. Espenson, *Inorganic Chemistry*, 1986, 25, 4108-4114.