Electronic Supporting Information

Recyclable and stable ruthenium catalyst for free radical polymerization at ambient temperature initiated by visible light photocatalysis

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1. General information

Methyl methacrylate (MMA, 99% Aldrich), butyl-methacrylate (BMA, 99% Aldrich), *tert*-butyl methacrylate (TBMA, 98% Aldrich), glycidyl methacrylate (GMA, 97%, Aldrich), 2-ethoxyethyl methacrylate (EEMA, 99% Aldrich), cyclohexyl methacrylate (CHMA, 97% Aldrich), isobutyl methacrylate (IBMA, 97% Aldrich), Ethyl methacrylate (EMA, 99% Aldrich) and benzyl methacrylate (96%, BZMA Aldrich) were purified three times through a column filled with basic alumina oxides. The purified monomers were stored at -20 ^{o}C and purged with high purity nitrogen prior to use. Ethyl 2-bromoisobutyrate (EBiB, 98%, Aldrich), N-N'-iso–dipropylethylamine ($^{i}Pr_2NEt$, 98%, Aldrich), Tris(bipyridine) ruthenium(II) dichloride hexahydrate ($Ru(bpy)_3Cl_2.6H_2O$, Aldrich), anhydrous N,N-dimethyl formamide (DMF, 99.5%, Aldrich), Nafion solution (5 wt.% solution in a mixture of alcohol and water, Aldrich) were used as received. Silica (fumed, with surface area 192 m^2/g) was washed with deionized water before use.

2. Procedure for preparation of ruthenium complex catalyst immobilized on nafion coated silica

Nafion coated silica (SiO_2/Nf) was prepared as follows. An aliquot (typically 0.8 ml) of nafion solution was added to the water washed SiO_2 powder (0.2 g), mixed well by sonication, and dried at 90 ^{o}C for 2 h. The obtained SiO_2/Nf powder (~0.24 g) was suspended in 20 ml aqueous solution of $Ru(bpy)_3^{2+}$ with different concentrations in a glass vial. Although SiO_2/Nf powder was not mixed well initially because of the hydrophobic nature of nafion, vigorous stirring for 2 h caused it to be well suspended in the solution. The suspension was stirred for 20 h at room temperature, and the solid powder was carefully recovered by filtration and washed with large amount of water until the filtrate was colorless. The obtained wet powder was dried at 80 ^{o}C for 10 h to get the final sample (SiO_2/Nf/RuL). As a control sample, ruthenium dye directly immobilized on silica (SiO_2/RuL) was prepared under the same procedure without adding the nafion polymer.

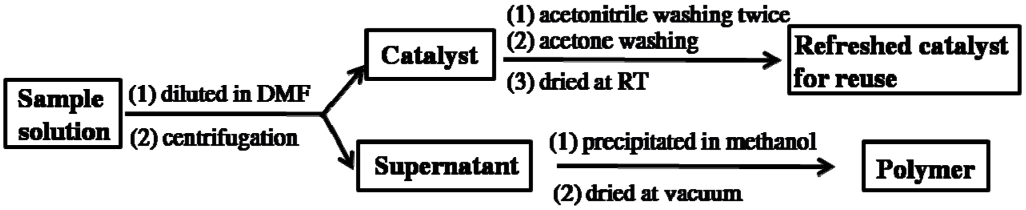
3. Characterization of immobilized catalysts

The immobilized catalysts were characterized as follows: The adsorbed amount of ruthenium dye on silica was calculated by the difference between initial dye concentration and dye concentration in the filtrate measured by the UV-Vis absorbance. The FT-IR spectra were recorded with pelletized samples on an FT-IR spectrophotometer (Bomem, MB104). The silica samples mixed with KBr powder were pelletized to a thin disk with a high-pressure pelletizer (Carver). Thermo-gravimetric analysis (TGA) of samples was also carried out for confirming the nafion and ruthenium dye loading. A thermo-gravimetric/ differential thermal analyzer (SII NanoTechnology Inc. EXSTRA6000 TG/DTA) was used in the temperature range of 20-600 ^{o}C with a heating rate of 4 ^{o}C/min under an air flow. High resolution transmission electron micrographs (HR-TEM) of various samples were recorded using a JEOL JEM-2100F microscope with Cs-corrected.

4. General procedure for polymerization of MMA

A Schlenk flask was charged with 2.5 mg SiO_2/Nf/RuL catalyst, sealed with rubber septum and was purged with nitrogen for 30 min to remove the oxygen. The degassed solvent CH_3CN (0.55 ml) and monomer MMA (0.55 mL, 5 mmol) was then added to the flask by using a syringe under protection of nitrogen. Then, $^{i}Pr_2NEt$ (42 μL, 0.25 mmol) and EBiB (19 uL, 0.125 mmol) were added under protection of nitrogen. Then, the flask was irradiated by a 27-W household fluorescent lamp. The temperature of the solution during irradiation was around 25 ^{o}C. After reaction, the viscous polymer solution was dissolved and diluted in small amount of DMF solution. The diluted polymer solution was centrifugated to recover solid catalyst. The solid catalyst was washed with acetonitrile twice and acetone one time for use in recyclability test. The solid polymer powder was obtained by precipitating part of supernatant polymer solution in large amount of methanol or water. The polymer was dried at vacuum overnight and the yields of polymers were calculated gravimetrically. The gel permeation chromatography (GPC) measurement determined the molecular weights (M_n and M_w) of the polymers. The GPC column system was calibrated with polystyrene standards, since the polystyrene standards have the similar molecular weight distributions with the synthesized polymer in this work. The chloroform was used as the solvent to dissolve polymer powder. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the centre line signal of the $CDCl_3$ triplet at 77.0 ppm. The abbreviations s, br. s, d, br. d, t, q, m, stand for the resonance multiplicity singlet, broad singlet, doublet, broad doublet, triplet, quartet and multiplet, respectively. To test the stability of nafion polymer during reaction, we have carried out the multiple cycle tests without adding of monomer and monitored the concentrations of sulfate and sulfite ions during the repeated cycles of photoinitiation of free radicals by IC (ion chromatography).

5. Scheme S1 Illustration of recovering process of immobilized catalyst for recycling test



6. **Table S1**. The adsorption parameters obtained by fitting the adsorption isotherm data with Langmuir adsorption model

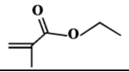
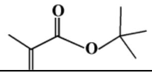
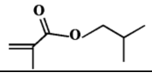
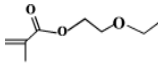
	[Dye]$_{mono}$ (mM)	[Dye]$_{mono}$ (umol)	Coverage Ratio (%)	K_{ad} (mM^{-1})
SiO_2/Nf/RuL	1.83	36.6	74.3	0.817
SiO_2/RuL	0.31	6.2	71.0	2.51

7. **Table S2** Control experiment of photocatalytic radical polymerization of methyl methacrylate

Entry	MMA	$^iPr_2NEt$	EBiB	Light	Catalyst	Y_P (%)
1	200	10	5	**no**	5 mg	0
2	200	10	5	yes	**0**	Trace
3	200	**0**	5	yes	5 mg	0
4	200	10	**0**	yes	5mg	0
5	200	10	5	yes	5mg	78

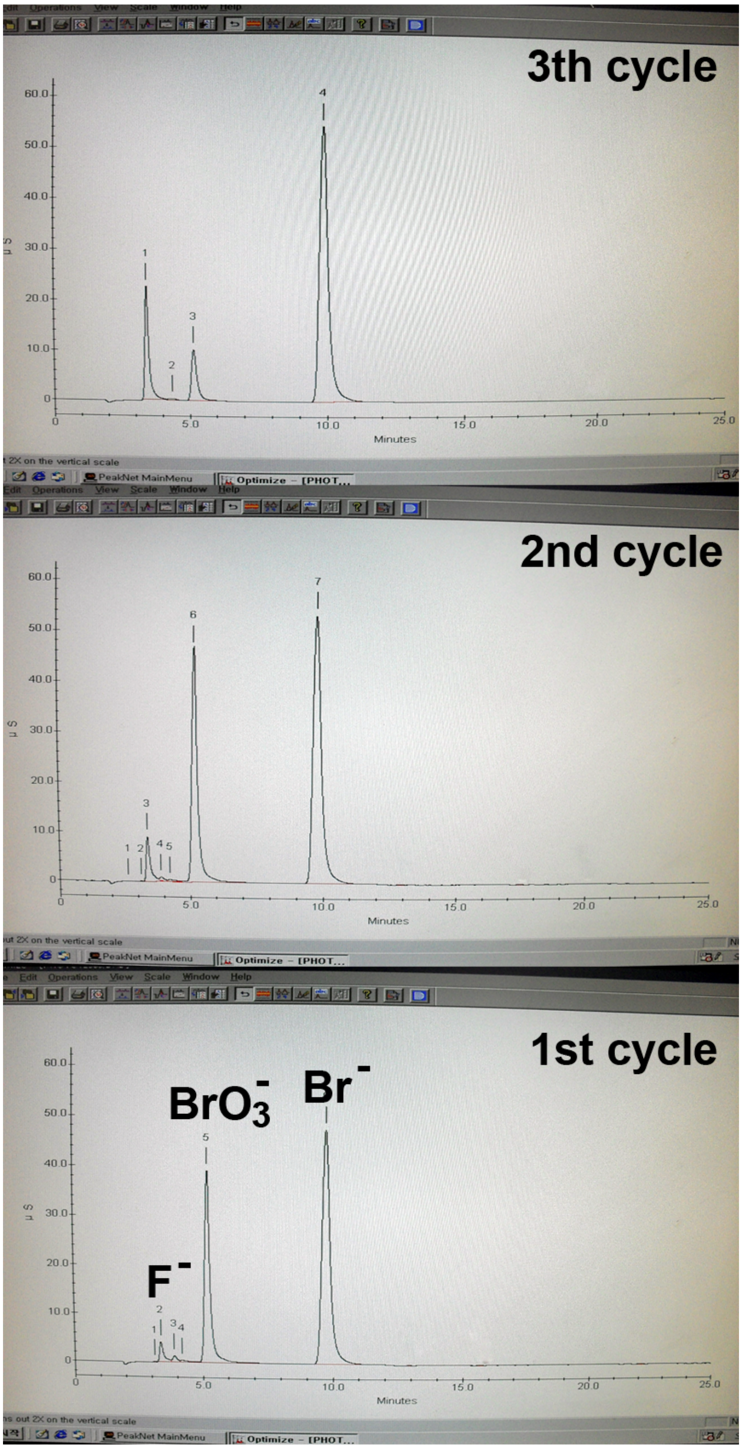
Conditions: 5 mmol MMA, MMA: ACN = 1:1(v/v), [MMA]: [EBiB]: [$^iPr_2NEt$] = 200:5:10, 27-W household fluorescent lamp (10 cm above the reactor) illuminated for 24 h. Y_P = produced polymer/polymer with 100% monomer conversion.

8. **Table S3.** Photocatalytic polymerization of methacrylates with different functional groups [a]

Entry	Monomer	Structure	Solvent	Catalyst (mg)	*Mn*	*Mw/Mn*	Y_P(%) [b]	Y_C [c]	TON [d]
1	EMA		acetonitrile	2.5	45400	2.0	78	2169	27.2
2	TBMA		acetonitrile	2.5	43200	2.0	70	2424	31.9
3	IBMA		acetonitrile	2.5	65500	1.8	75	2597	22.6
4	EEMA		acetonitrile	2.5	52300	3.0	86	3314	36.1

[a] Reaction conditions: 5 mmol monomer, monomer: Solvent = 1:1(v/v), [monomer]: [EBiB]: [$^iPr_2NEt$] = 200:5:10, 27-W fluorescent lamp (10 cm above the reactor) illuminated for 24 h. [b] Y_P = produced polymer / polymer with 100% monomer conversion; [c] Y_C= produced polymer (mg) / input RuL catalyst (mg). [d] Turnover number (TON) = no. initiated radicals / no. of immobilized RuL molecules.

9. Figure S1. Ion chromatography analysis of sample solutions during repeated photoinitiation cycles



10. ^{1}H and ^{13}C NMR spectra of synthesized polymer

PMMA $^{1-3)}$ **(Table 1, entry 5):** [MMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, MMA: ACN = 1: 1 (v/v), 2.5 mg catalyst, visible light irradiation **24 h**, yield = **75%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 3.72 (br. s, 3H), 1.90-2.04 (m, 2H), 0.90-1.00 (t, 3H);

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 54.2, 51.8, 44.6, 16.5.

PBMA $^{4-6)}$ **(Table 1, entry 7):** [BMA] : [EBiB]: [^{i}Pr$_2$NEt] = 200 : 5 : 10, BMA: ACN = 1: 1 (v/v), 2.5 mg catalyst , visible light irradiation 24 **h**, yield = **70%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 3.96 (t, 2H), 1.78-1.92 (m, 2H), 1.63(m, 2H), 1.41 (m, 2H), 0.96 (t, 3H), 0.94-1.04(t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 64.7, 54.2, 45.0, 30.2, 19.3, 16.5, 13.9

PCHMA $^{7)}$ **(Table 1, entry 8):** [CHMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, CHMA: ACN = 1: 1 (v/v), 2.5 mg catalyst , visible light irradiation **24 h**, yield = **85%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 4.67(s, 1H), 1.80-1.95 (m, 2H), 1.30-1.60 (m, 6H), 0.89-1.07 (t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 73.2, 54.0, 45.5, 31.8, 29.2, 25.4, 18.2.

PBZMA $^{7)}$ **(Table 1, entry 9):** [BZMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, BZMA: ACN = 1: 1 (v/v), 2.5 mg catalyst, visible light irradiation **24 h**, yield = **84%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 7.29(br. s, 5H), 4.91 (br. s, 2H), 1.90-2.00 (m, 2H), 0.77-0.95(t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 135.1, 130.1, 128.4, 127.7, 66.7, 54.4, 45.1, 16.4

PGMA $^{8,9)}$ **(Table 1, entry 10):** [GMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, GMA: ACN = 1: 1 (v/v), 2.5 mg catalyst, visible light irradiation **24 h**, yield = **92%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 3.83-4.31(d, 2H), 3.24 (m, 1H), 2.65-2.90(d, 2H), 1.97-2.10 (m, 2H), 0.95- (t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.3, 65.8, 54.1, 48.9, 48.8, 44.6, 16.8

PEMA [1-3] (Table S3, entry 1): [EMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5: 10, EMA: ACN = 1: 1 (v/v), 2.5 mg catalyst, visible light irradiation **24 h**, yield = **78%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 4.05(q, 2H), 1.95-2.05 (m, 2H), 1.39 (t, 3H), 0.95-1.05(t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 60.8, 54.2, 45.1, 18.6, 13.9.

PTBMA [4-6] (Table S3, entry 2): [TBMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, TBMA: ACN = 1: 1 (v/v), 2.5 mg catalyst ,visible light irradiation **24 h**, yield = **70%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 1.73-1.81 (t, 2H), 1.37(br. S, 9H), 0.94-1.04 (t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 80.8, 54.7, 40.1, 27.7, 17.7

PIBMA [4-6] (Table S3, entry 3): [IBMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, IBMA: ACN = 1: 1 (v/v), 2.5 mg catalyst , visible light irradiation **24 h**, yield = **75%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 3.72 (d, 2H), 1.85-1.95 (m, 2H), 1.05(s, 1H), 0.98(br. d, 6H), 0.90 -1.04(t, 3H)

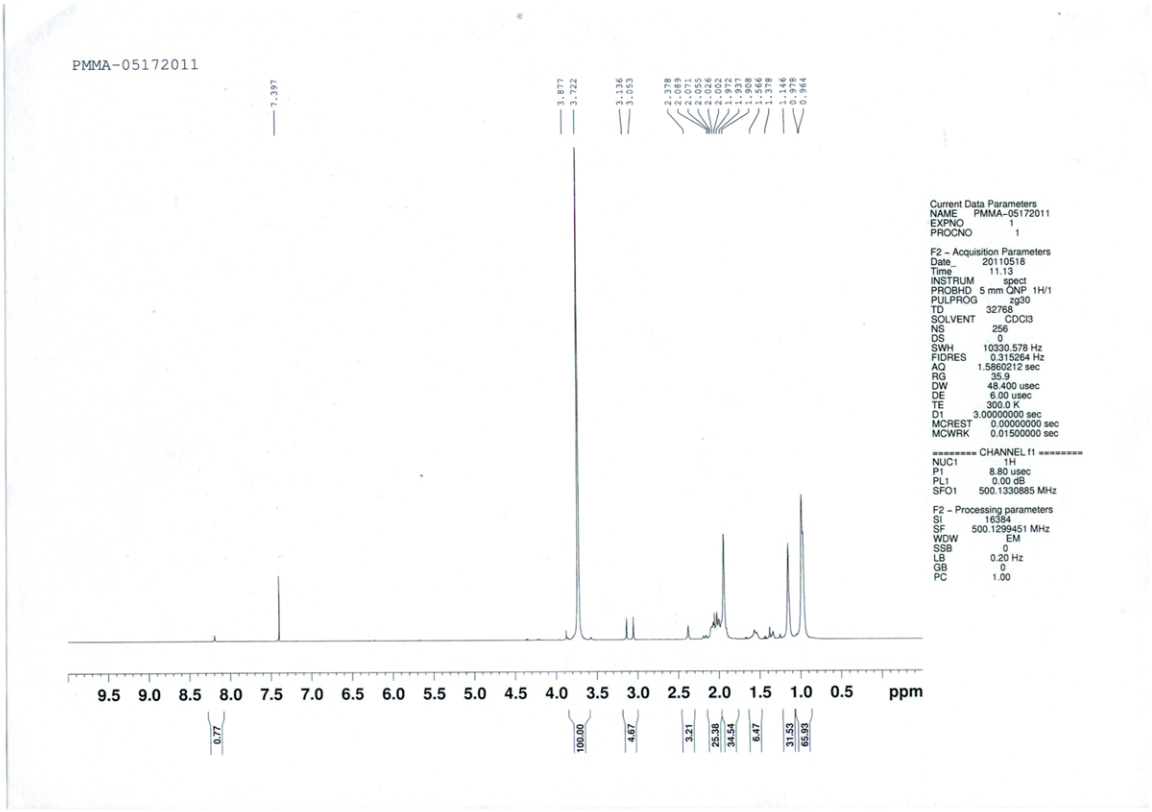
^{13}C-NMR (CDCl$_3$, 125 MHz): 177.7, 71.1, 54.7, 45.1, 29.5, 19.3, 16.4.

PEEMA [8,9] (Table S3, entry 4): [TBMA] : [EBiB] : [^{i}Pr$_2$NEt] = 200 : 5 : 10, EEMA: ACN = 1: 1 (v/v), 2.5 mg catalyst , visible light irradiation **24 h**, yield = **86%**.

^{1}H-NMR (CDCl$_3$, 500 MHz): 4.09(t, 2H), 3.53(t, 2H), 3.50(t, 2H), 1.94-2.04(m, 2H), 1.22(t, 3H), 0.95 (t, 3H)

^{13}C-NMR (CDCl$_3$, 125 MHz): 177.6, 67.7, 66.5, 63.9, 54.1, 17.3, 13.4.

PMMA (Table 1, entry 5)



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NS                256
DS                  0
SWH        10330.578 Hz
FIDRES      0.315264 Hz
AQ         1.5860212 sec
RG               35.9
DW             48.400 usec
DE               6.00 usec
TE              300.0 K
D1         3.00000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

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PL1              0.00 dB
SFO1      500.1330885 MHz

F2 - Processing parameters
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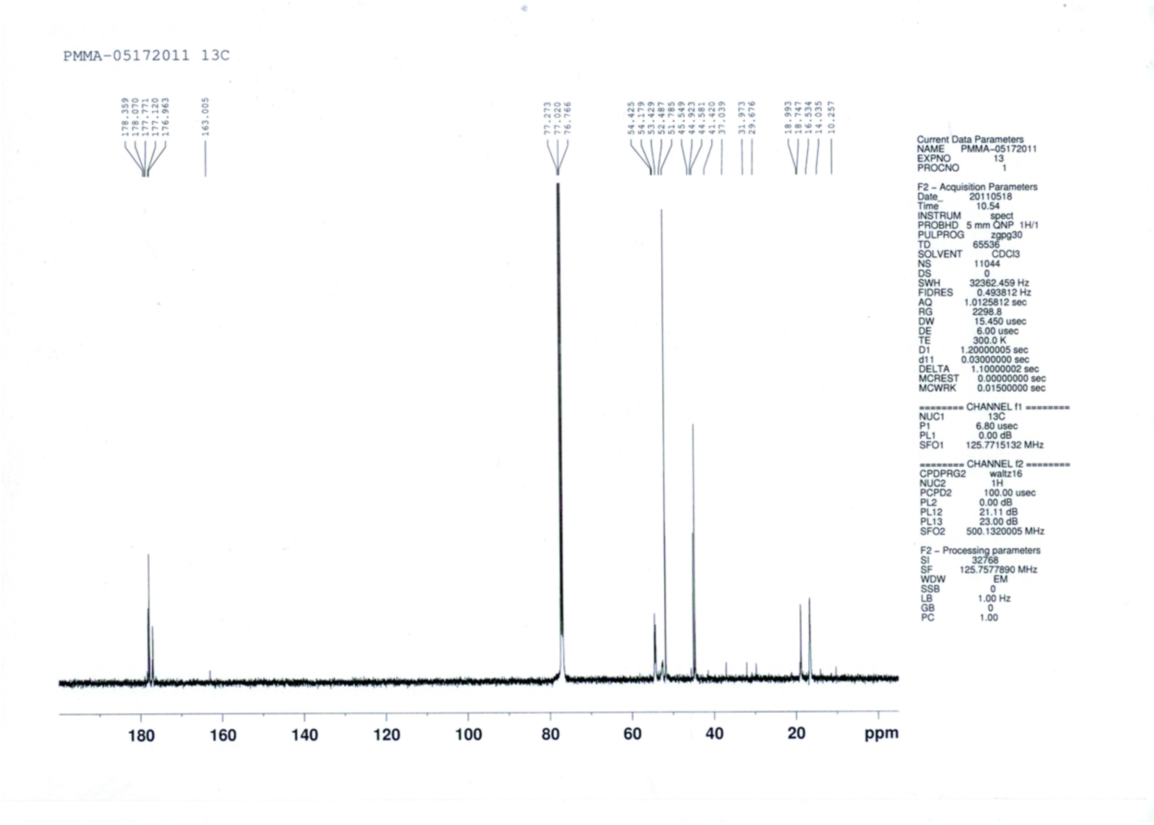
Figure S1. ^{1}H-NMR spectrum of PMMA



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DE               6.00 usec
TE              300.0 K
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d11        0.03000000 sec
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MCWRK      0.01500000 sec

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PL1              0.00 dB
SFO1      125.7715132 MHz

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NUC2               1H
PCPD2          100.00 usec
PL2              0.00 dB
PL12            21.11 dB
PL13            23.00 dB
SFO2      500.1320005 MHz

F2 - Processing parameters
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SF        125.7577890 MHz
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LB               1.00 Hz
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PC               1.00
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Figure S2. ^{13}C-NMR spectrum of PMMA

PBMA (Table 1, entry 7)

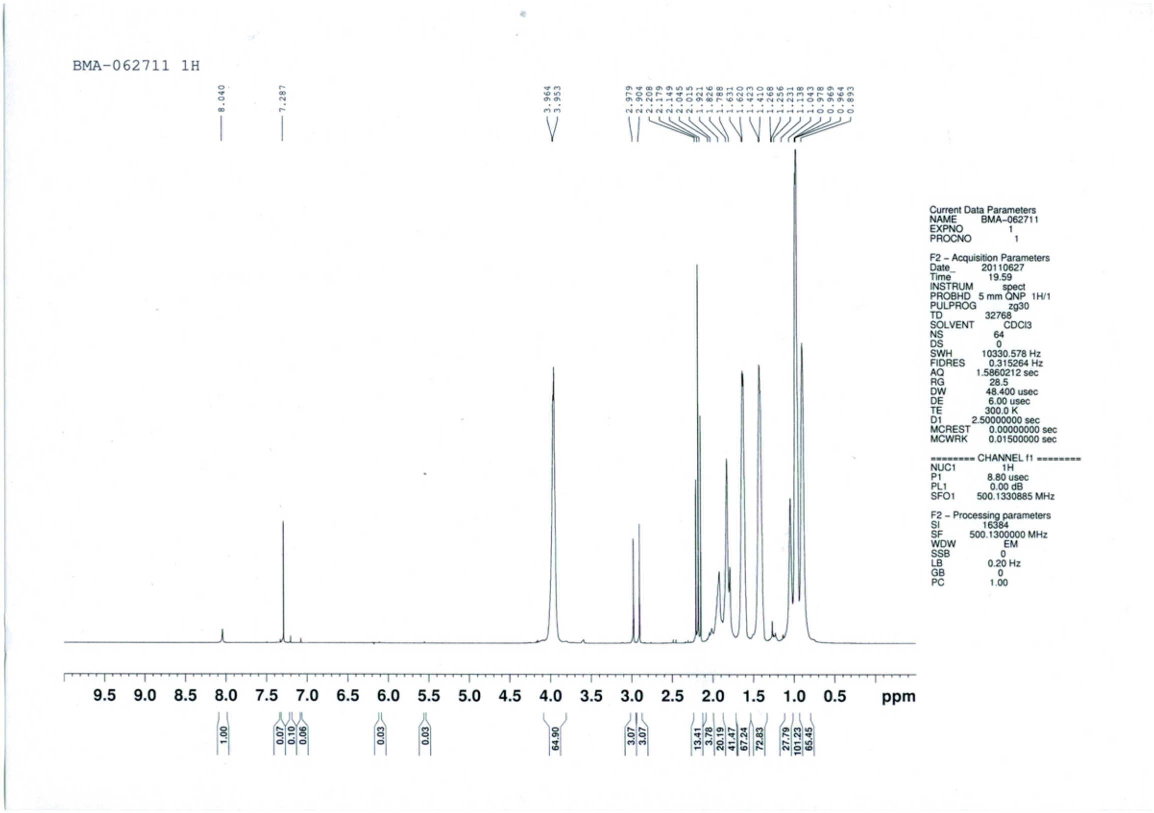


Figure S3. ^{1}H-NMR spectrum of PBMA

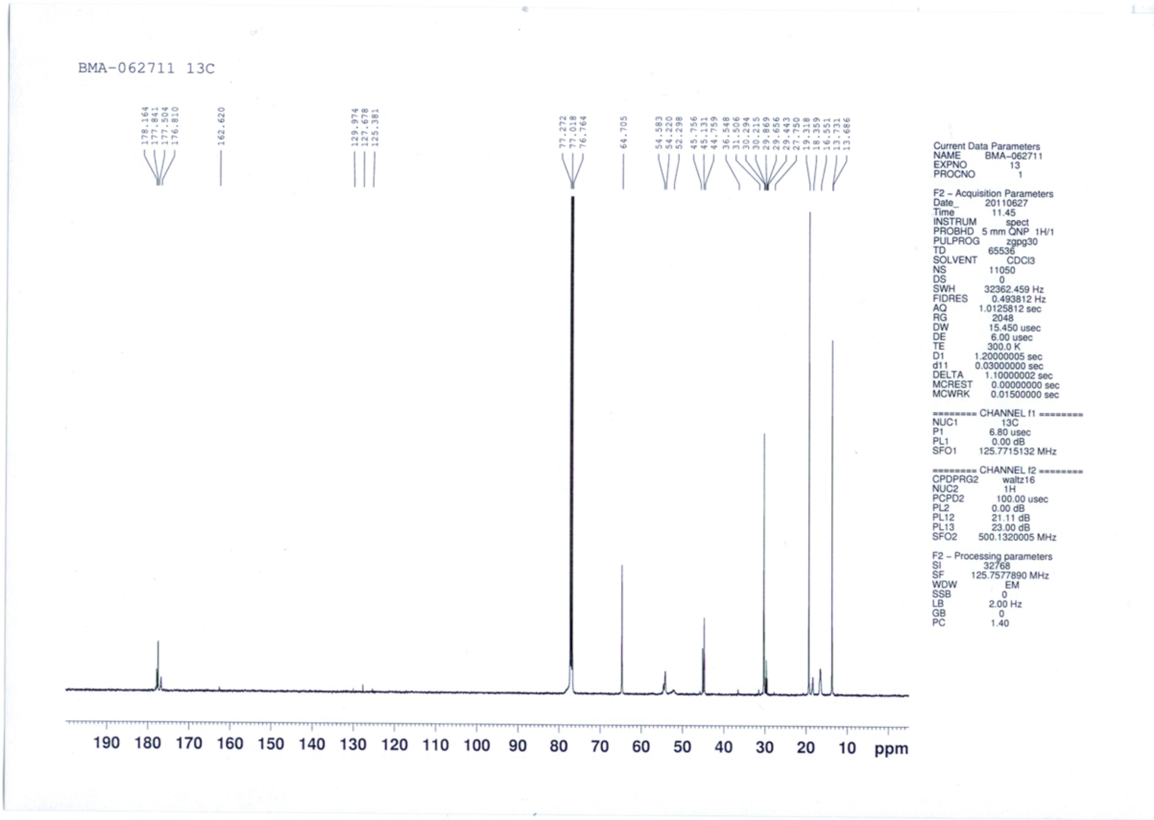
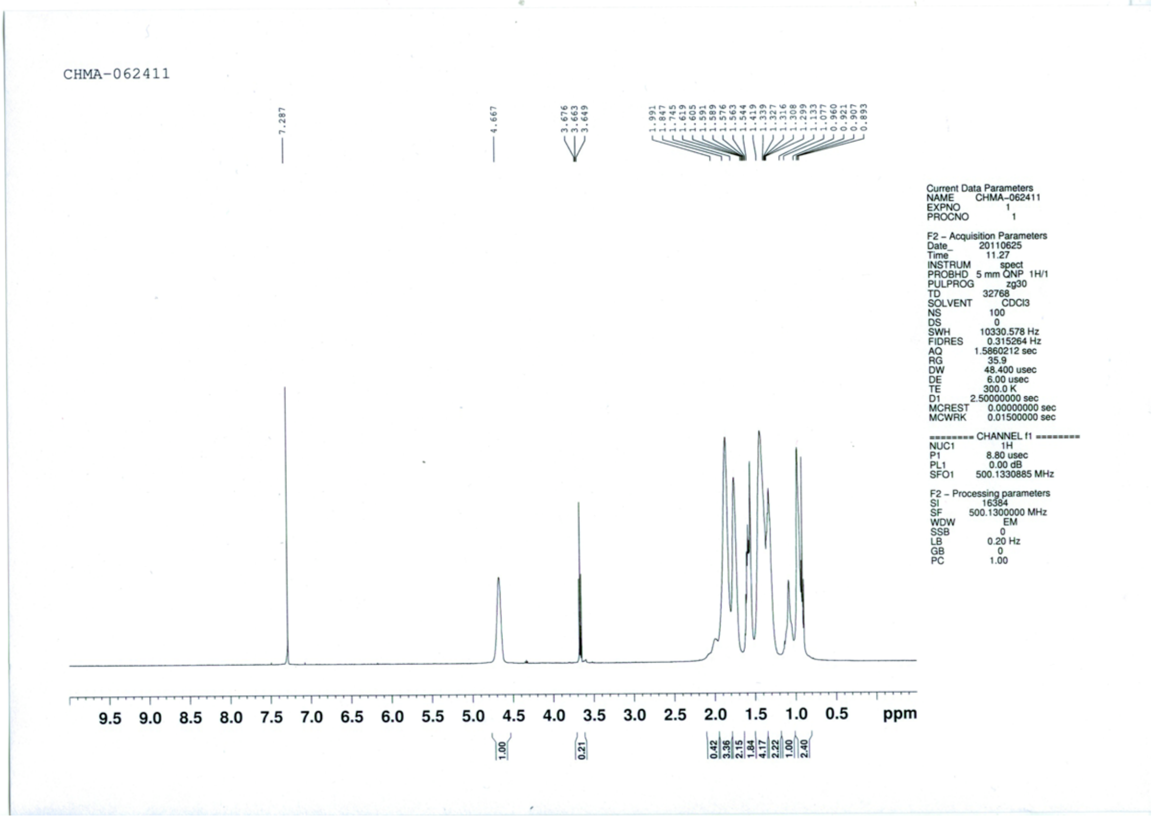


Figure S4. ^{13}C-NMR spectrum of PBMA

PCHMA (Table 1, entry 8)



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SOLVENT         CDCl3
NS                100
DS                  0
SWH      10330.578 Hz
FIDRES    0.315264 Hz
AQ       1.5860212 sec
RG               35.9
DW         48.400 usec
DE           6.00 usec
TE            300.0 K
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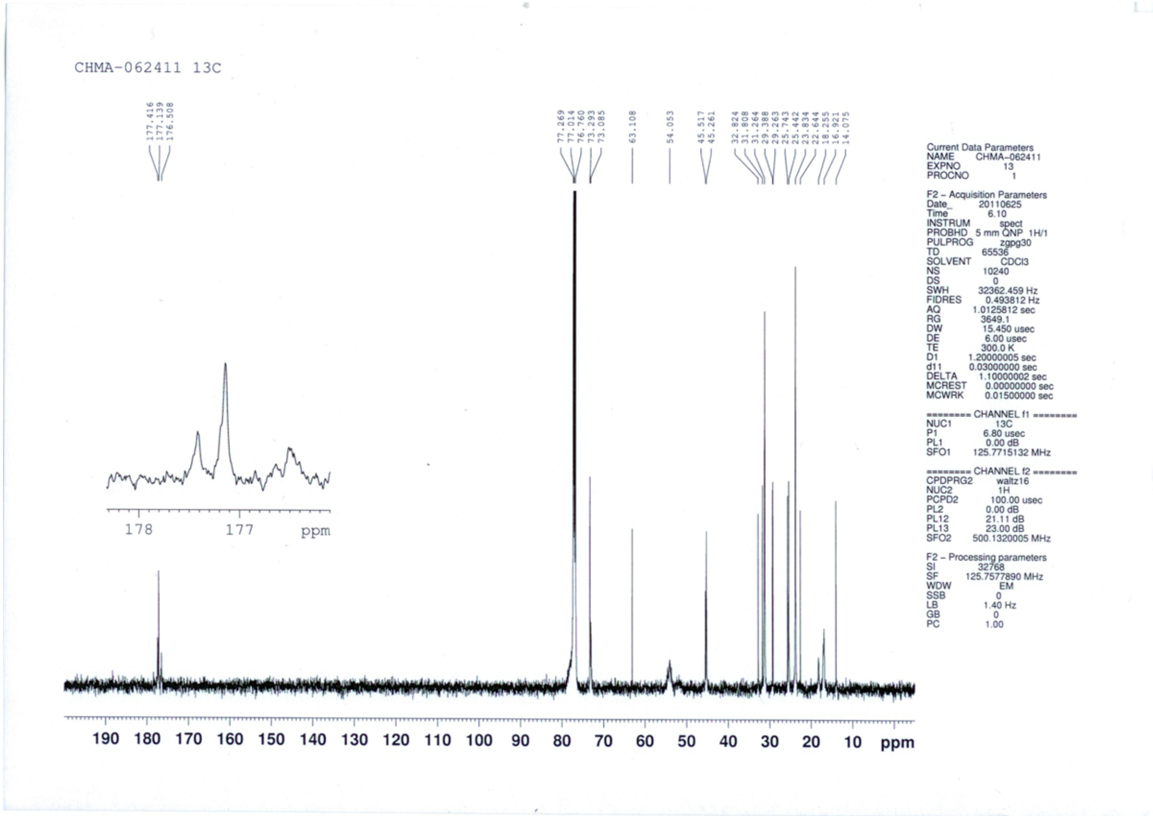
Figure S5. ^{1}H-NMR spectrum of PCHMA



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TD              65536
SOLVENT         CDCl3
NS              10240
DS                  0
SWH      32362.459 Hz
FIDRES    0.493812 Hz
AQ       1.0125812 sec
RG             3649.1
DW         15.450 usec
DE           6.00 usec
TE            300.0 K
D1      1.20000005 sec
d11     0.03000000 sec
DELTA   1.10000002 sec
MCREST  0.00000000 sec
MCWRK   0.01500000 sec

======== CHANNEL f1 ========
NUC1              13C
P1          6.80 usec
PL1           0.00 dB
SFO1   125.7715132 MHz

======== CHANNEL f2 ========
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NUC2               1H
PCPD2     100.00 usec
PL2           0.00 dB
PL12         21.11 dB
PL13         23.00 dB
SFO2   500.1320005 MHz

F2 - Processing parameters
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WDW                EM
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Figure S6. ^{13}C-NMR spectra of PCHMA

PBZMA (Table 1, entry 9)

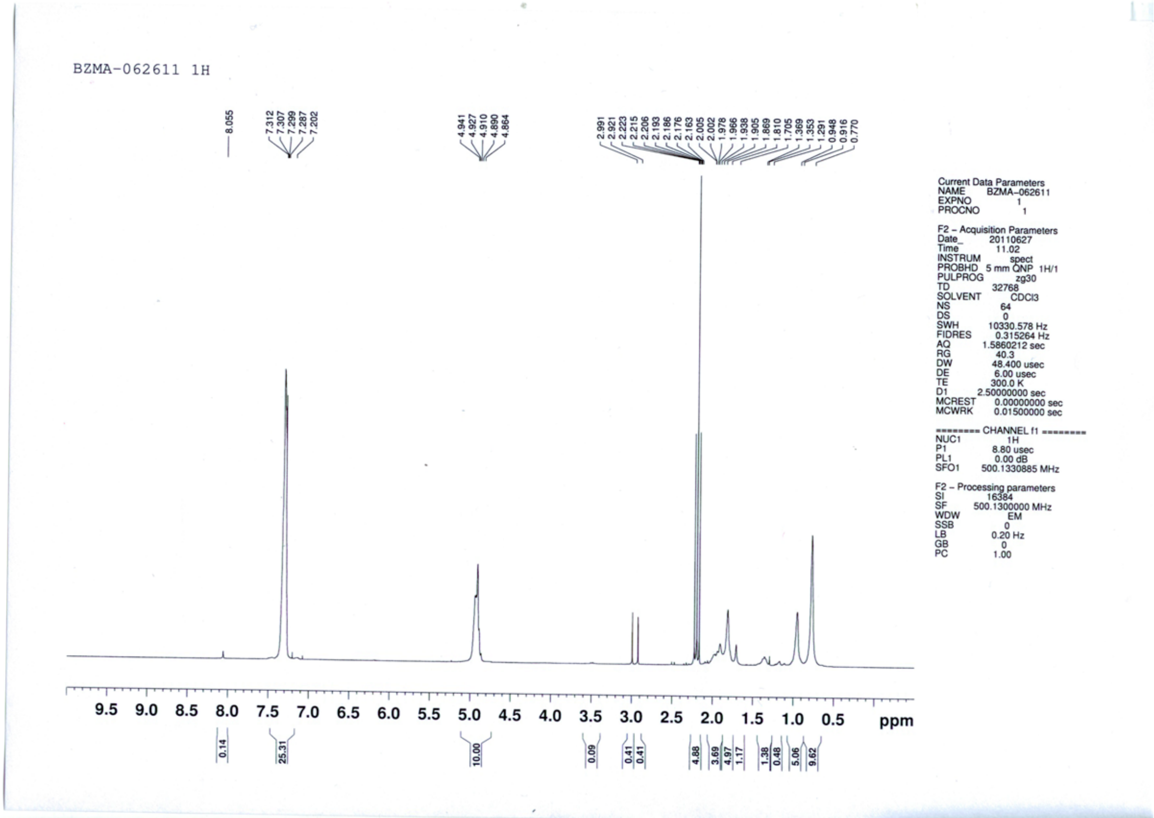


Figure S7. ^{1}H-NMR spectrum of PBZMA

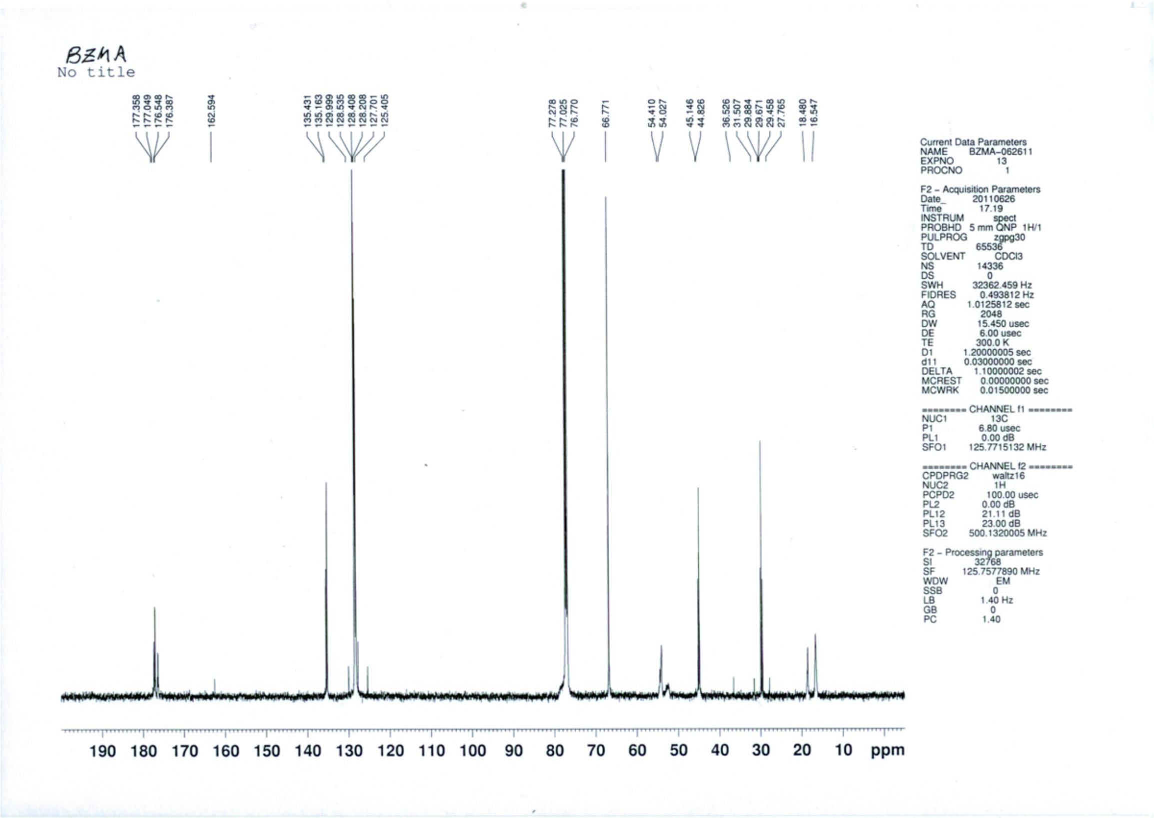
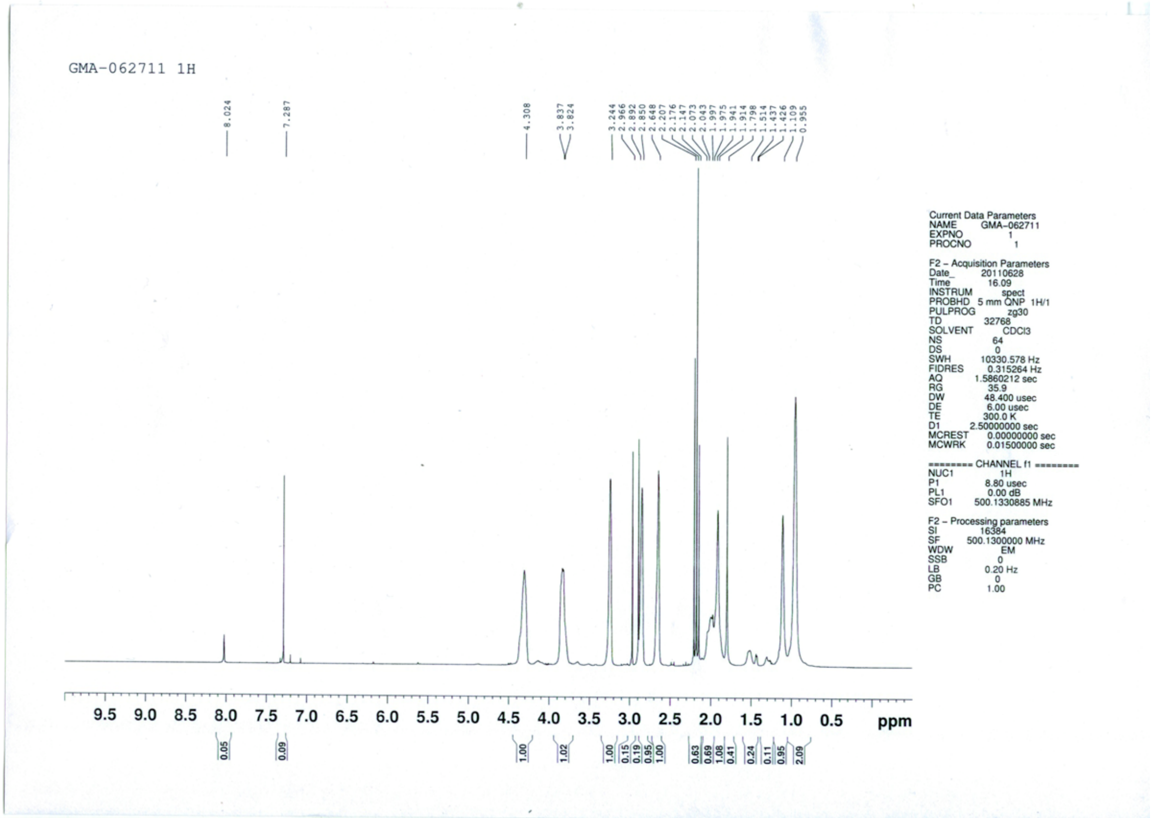


Figure S8. ^{13}C-NMR spectrum of PBZMA

PGMA (Table 1, entry10)



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DS                0
SWH        10330.578 Hz
FIDRES      0.315264 Hz
AQ         1.5860212 sec
RG               35.9
DW            48.400 usec
DE              6.00 usec
TE             300.0 K
D1        2.50000000 sec
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P1              8.80 usec
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F2 - Processing parameters
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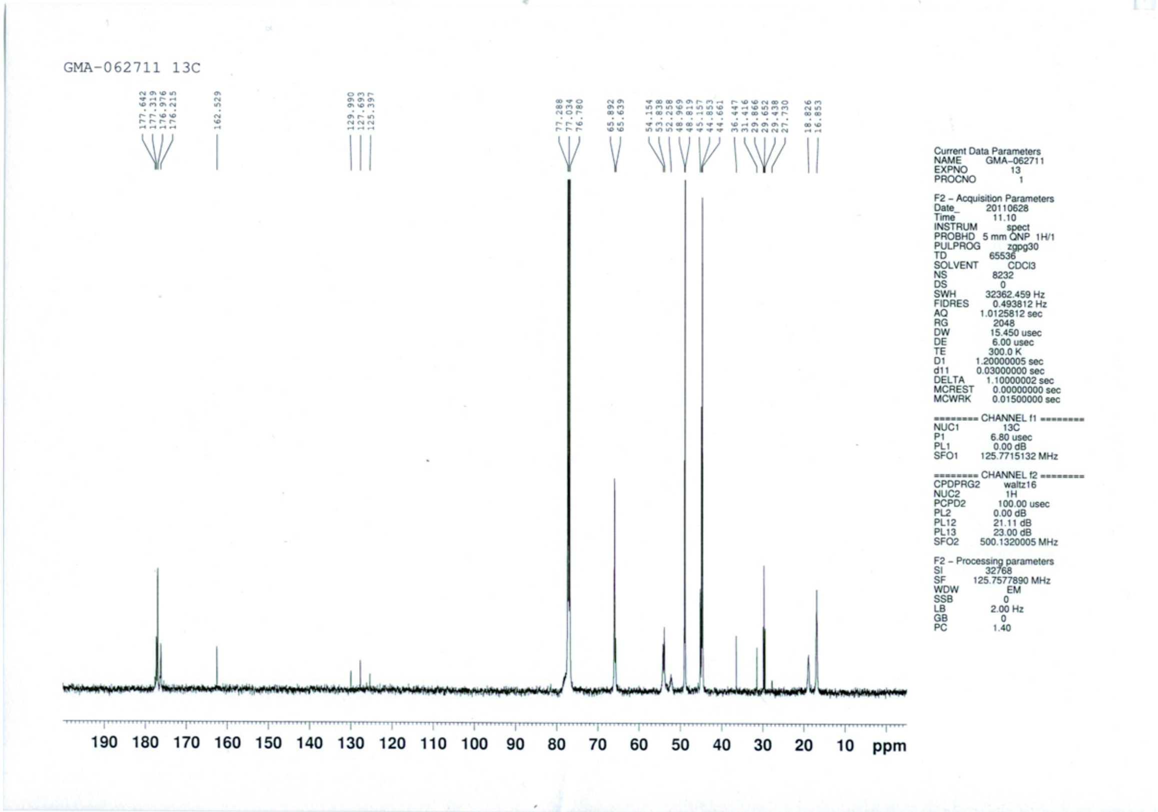
Figure S9. ^{1}H-NMR spectrum of PGMA



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PROCNO             1

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SWH        32362.459 Hz
FIDRES      0.493812 Hz
AQ         1.0125812 sec
RG              2048
DW            15.450 usec
DE              6.00 usec
TE             300.0 K
D1        1.20000005 sec
d11       0.03000000 sec
DELTA     1.10000002 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1             13C
P1              6.80 usec
PL1             0.00 dB
SFO1     125.7715132 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2              1H
PCPD2         100.00 usec
PL2             0.00 dB
PL12           21.11 dB
PL13           23.00 dB
SFO2     500.1320005 MHz

F2 - Processing parameters
SI             32768
SF       125.7577890 MHz
WDW               EM
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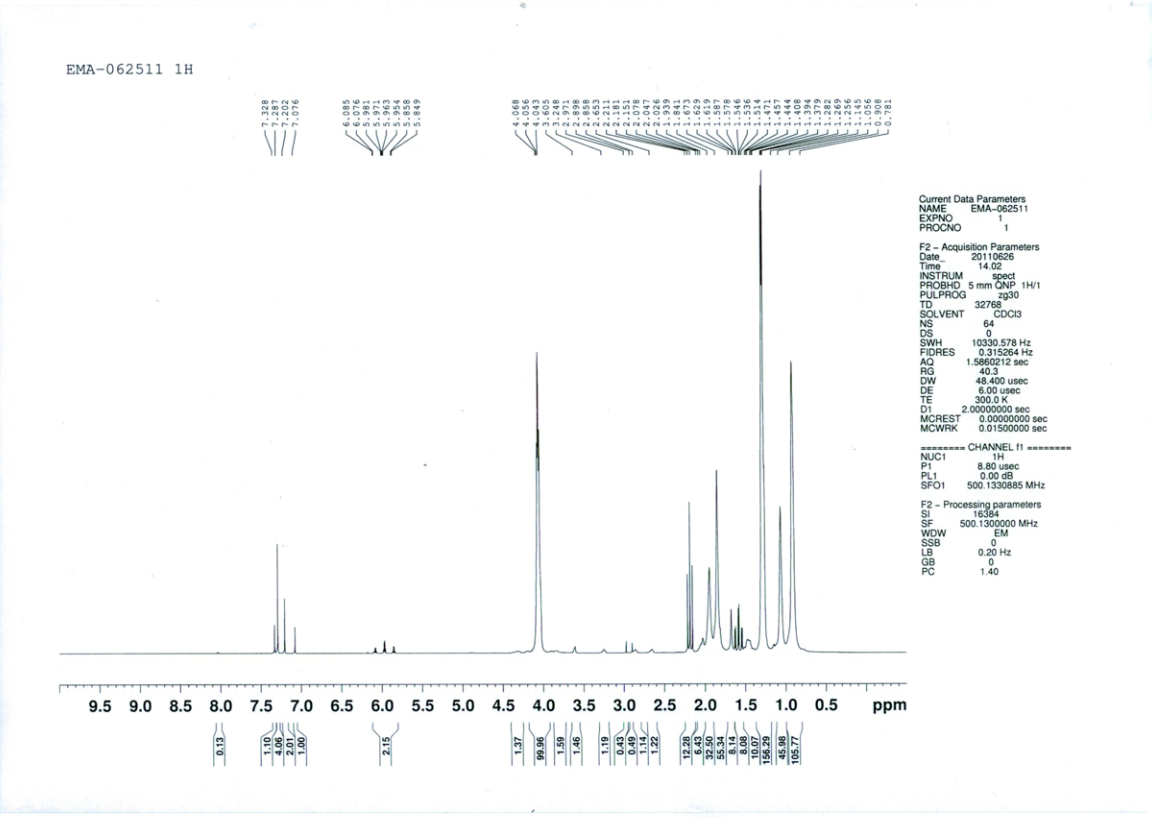
Figure S10. ^{13}C-NMR spectrum of PGMA

PEMA (Table S3, entry 1)



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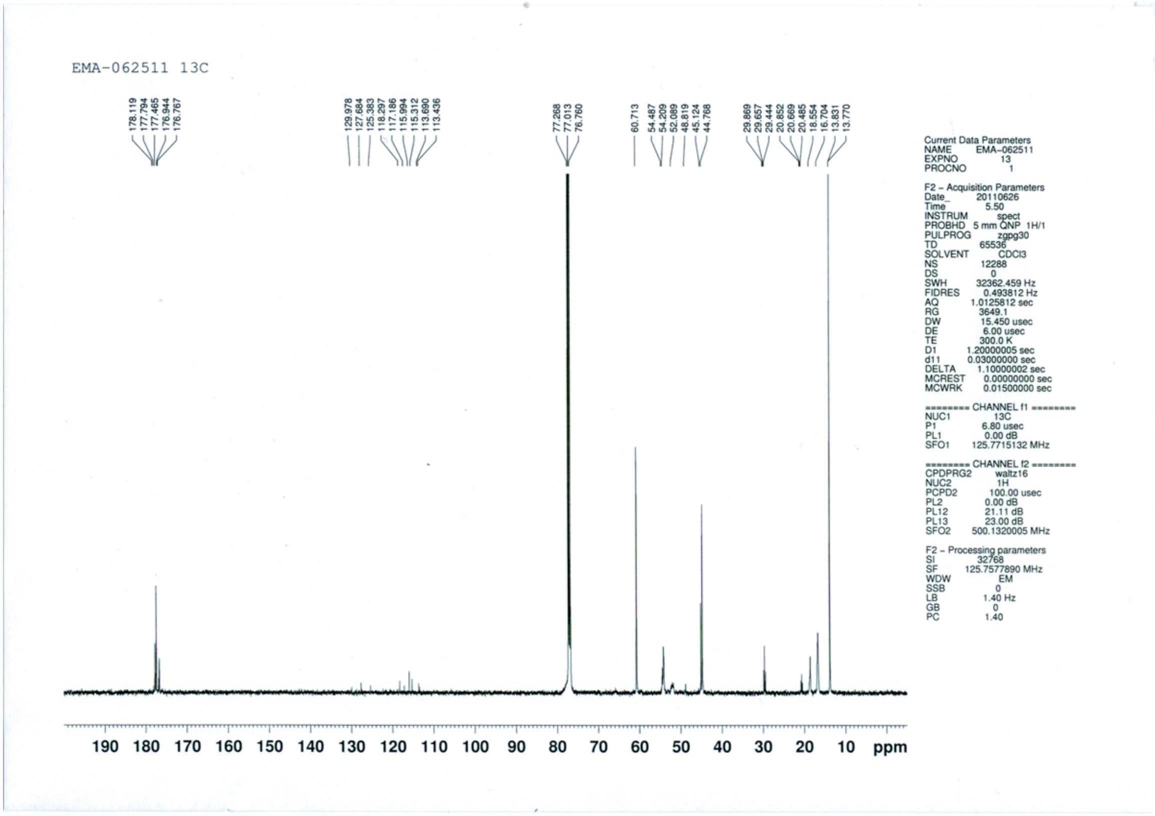
Time          14.02
INSTRUM        spect
PROBHD  5 mm QNP  1H/1
PULPROG         zg30
TD           32768
SOLVENT        CDCl3
NS              64
DS               0
SWH        10330.578 Hz
FIDRES      0.315264 Hz
AQ         1.5860212 sec
RG              40.3
DW          48.400 usec
DE            6.00 usec
TE           300.0 K
D1       2.00000000 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1            1H
P1           8.80 usec
PL1           0.00 dB
SFO1     500.1330885 MHz

F2 - Processing parameters
SI           16384
SF      500.1300000 MHz
WDW             EM
SSB              0
LB           0.20 Hz
GB               0
PC            1.40
```

Figure S11. ^{1}H-NMR spectrum of PEMA



```
Current Data Parameters
NAME       EMA-062511
EXPNO          13
PROCNO          1

F2 - Acquisition Parameters
Date_       20110626
Time           5.50
INSTRUM        spect
PROBHD  5 mm QNP  1H/1
PULPROG       zgpg30
TD           65536
SOLVENT        CDCl3
NS           12288
DS               0
SWH        32362.459 Hz
FIDRES      0.493812 Hz
AQ         1.0125812 sec
RG            3649.1
DW          15.450 usec
DE            6.00 usec
TE           300.0 K
D1       1.20000005 sec
d11      0.03000000 sec
DELTA    1.10000002 sec
MCREST    0.00000000 sec
MCWRK     0.01500000 sec

======== CHANNEL f1 ========
NUC1           13C
P1           6.80 usec
PL1           0.00 dB
SFO1     125.7715132 MHz

======== CHANNEL f2 ========
CPDPRG2      waltz16
NUC2            1H
PCPD2       100.00 usec
PL2           0.00 dB
PL12         21.11 dB
PL13         23.00 dB
SFO2     500.1320005 MHz

F2 - Processing parameters
SI           32768
SF      125.7577890 MHz
WDW             EM
SSB              0
LB           1.40 Hz
GB               0
PC            1.40
```

Figure S12. ^{13}C-NMR spectrum of PEMA

PTBMA (Table S3, entry 2)

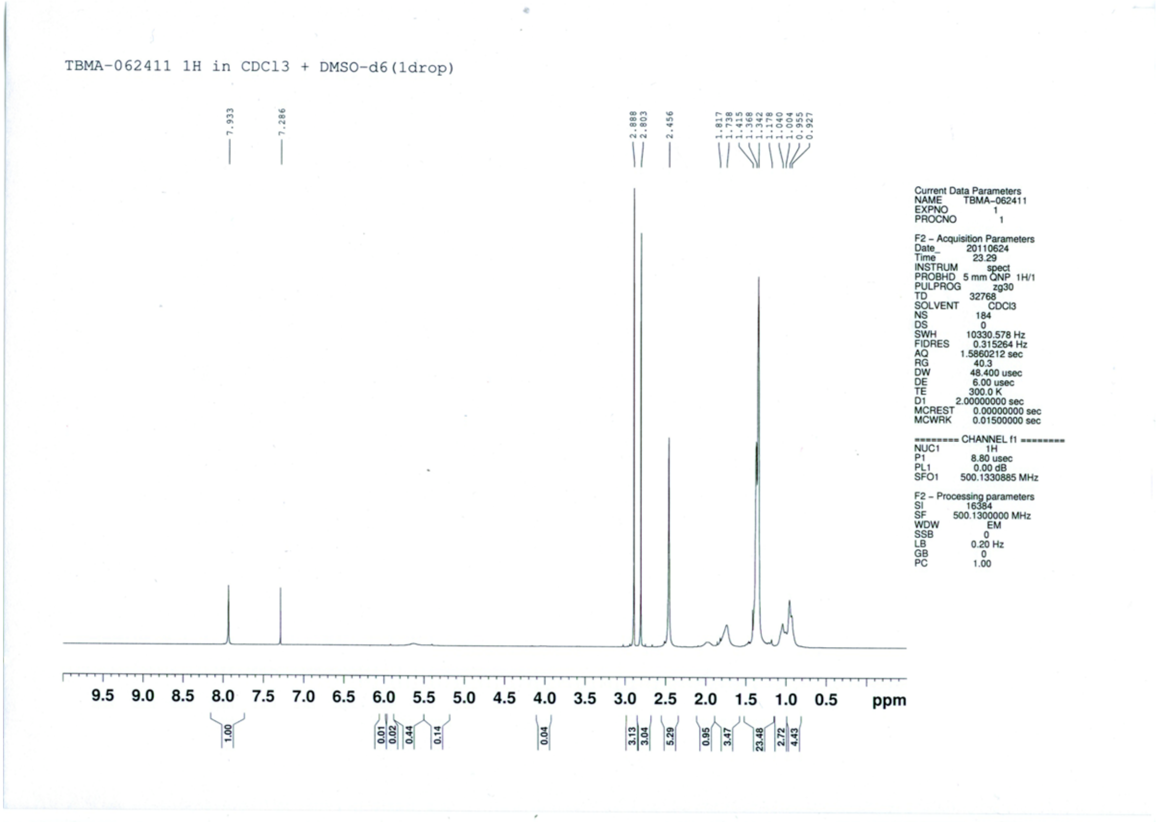


Figure S13. ^{1}H-NMR spectrum of PTBMA

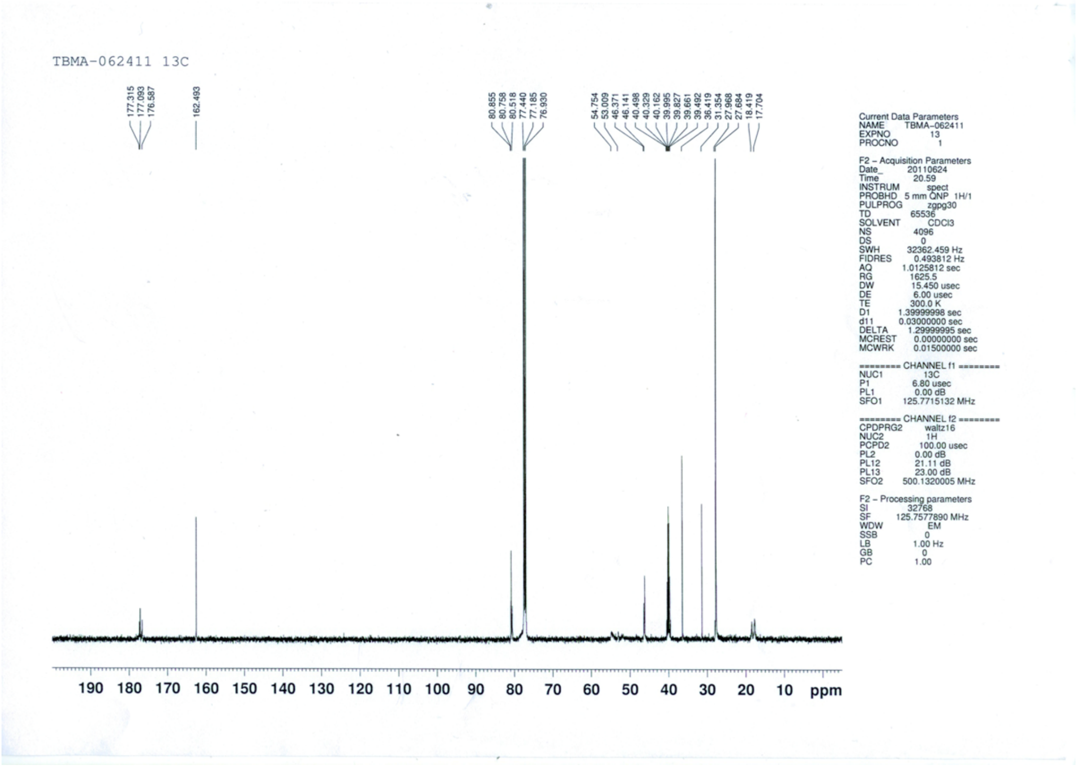


Figure S14. ^{13}C-NMR spectrum of PTBMA

PIBMA (Table S3, entry 3)

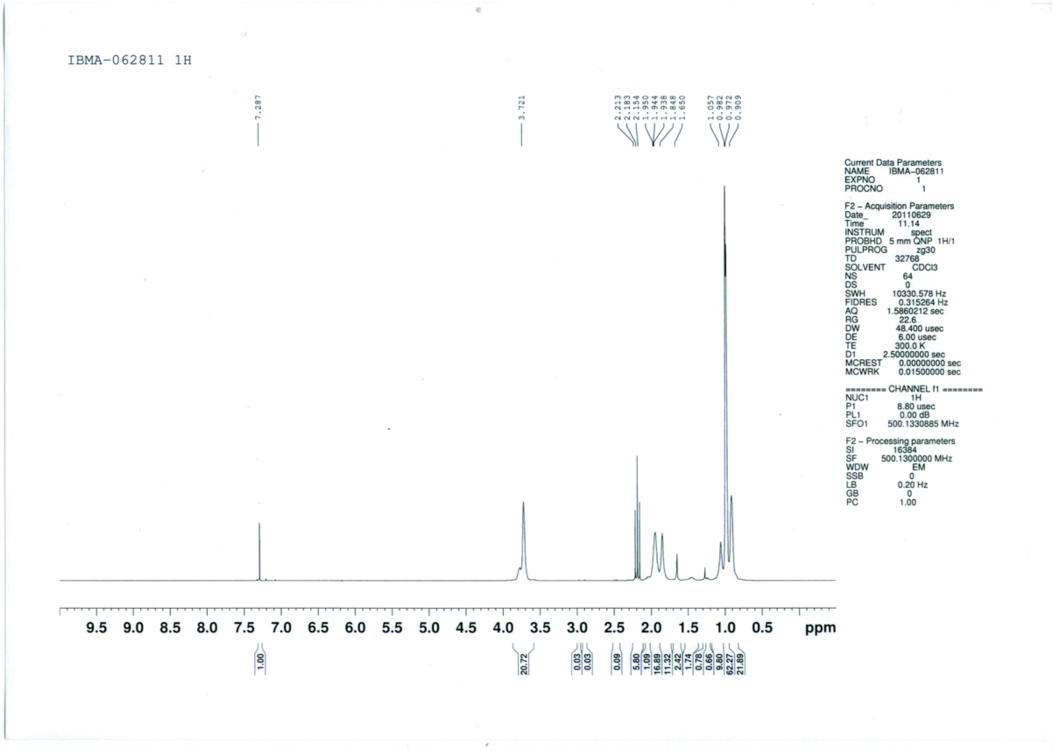


Figure S15. ^{1}H-NMR spectrum of PIBMA

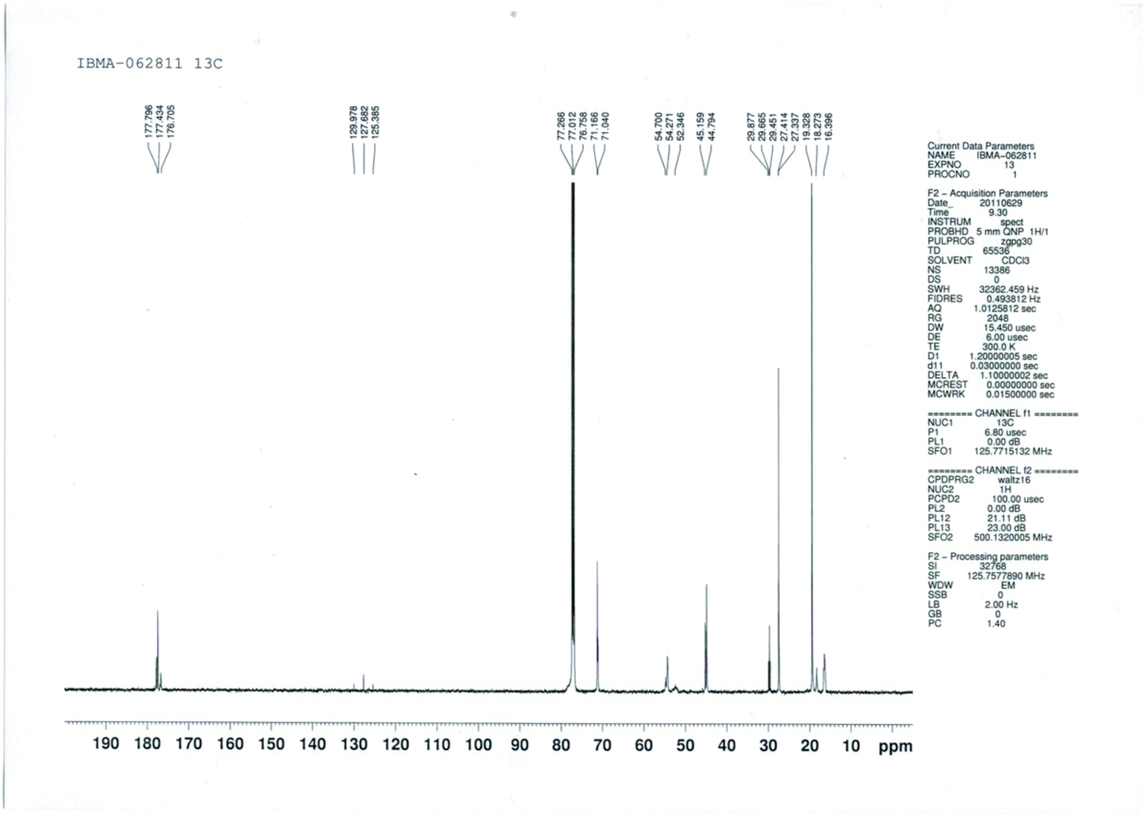
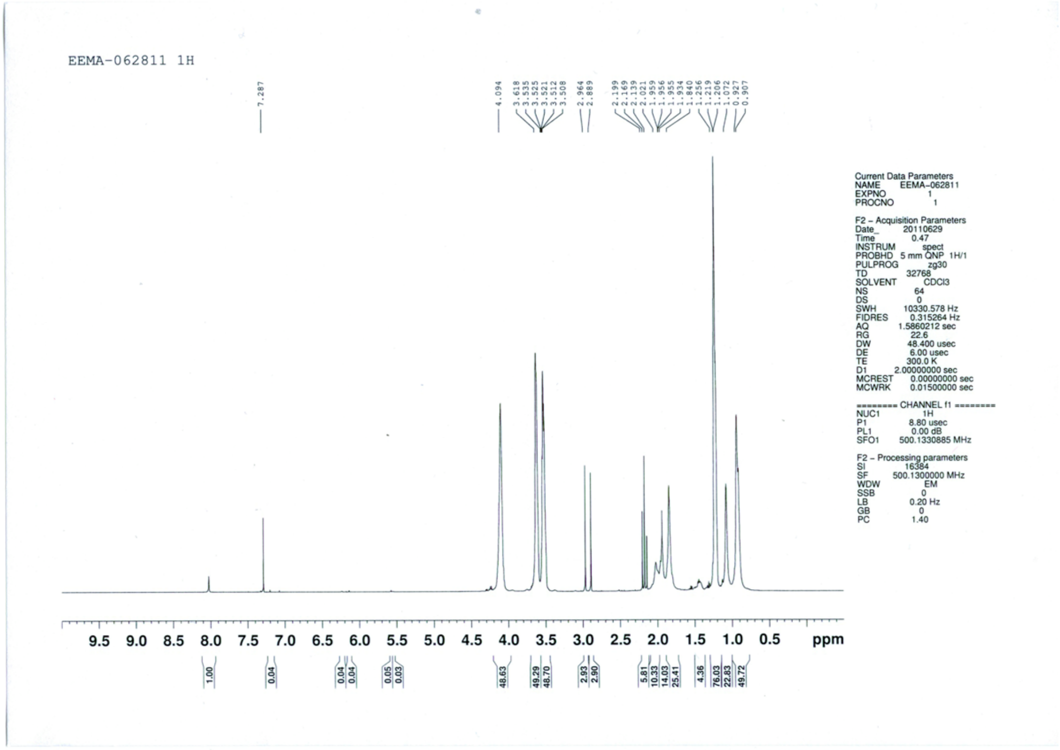


Figure S16. ^{13}C-NMR spectrum of PIBMA

PEEMA (Table S3, entry4)



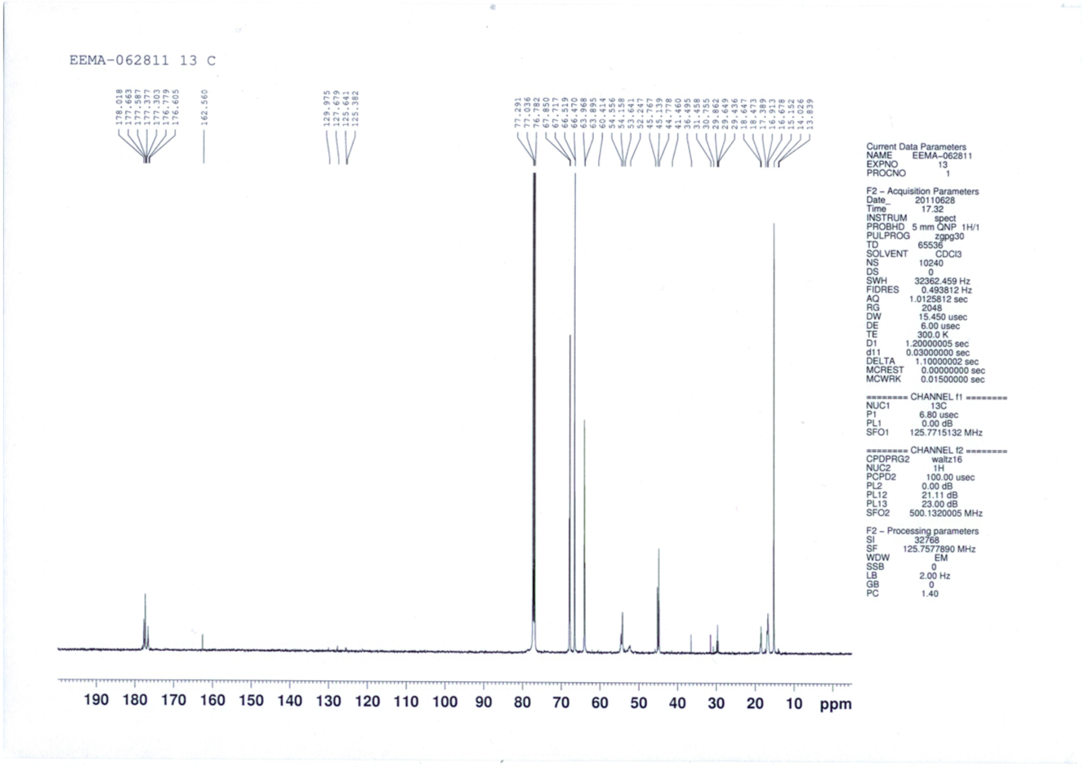
```
Current Data Parameters
NAME       EEMA-062811
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20110629
Time           0.47
INSTRUM        spect
PROBHD   5 mm QNP 1H/1
PULPROG        zg30
TD            32768
SOLVENT        CDCl3
NS               64
DS                0
SWH       10330.578 Hz
FIDRES     0.315264 Hz
AQ        1.5860212 sec
RG             22.6
DW           48.400 usec
DE             6.00 usec
TE            300.0 K
D1       2.00000000 sec
MCREST   0.00000000 sec
MCWRK    0.01500000 sec

======== CHANNEL f1 ========
NUC1             1H
P1             8.80 usec
PL1            0.00 dB
SFO1    500.1330885 MHz

F2 - Processing parameters
SI            16384
SF      500.1300000 MHz
WDW              EM
SSB               0
LB             0.20 Hz
GB                0
PC             1.40
```

Figure S17. ^{1}H-NMR spectrum of PEEMA



```
Current Data Parameters
NAME       EEMA-062811
EXPNO             13
PROCNO             1

F2 - Acquisition Parameters
Date_       20110628
Time          17.32
INSTRUM        spect
PROBHD   5 mm QNP 1H/1
PULPROG      zgpg30
TD            65536
SOLVENT        CDCl3
NS            10240
DS                0
SWH       32362.459 Hz
FIDRES     0.493812 Hz
AQ        1.0125812 sec
RG             2048
DW           15.450 usec
DE             6.00 usec
TE            300.0 K
D1       1.20000005 sec
d11      0.03000000 sec
DELTA    1.10000002 sec
MCREST   0.00000000 sec
MCWRK    0.01500000 sec

======== CHANNEL f1 ========
NUC1            13C
P1             6.80 usec
PL1            0.00 dB
SFO1    125.7715132 MHz

======== CHANNEL f2 ========
CPDPRG2     waltz16
NUC2             1H
PCPD2        100.00 usec
PL2            0.00 dB
PL12          21.11 dB
PL13          23.00 dB
SFO2    500.1320005 MHz

F2 - Processing parameters
SI            32768
SF      125.7577890 MHz
WDW              EM
SSB               0
LB             2.00 Hz
GB                0
PC             1.40
```

Figure S18. ^{13}C-NMR spectra of PEEMA

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