

## Supplementary Information

### Highly Efficient Access to Well-Defined Linear Polymers with Substantial Vinyl Pendants via ATRP of Divinyl Monomers

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## Contents

1. General Information .....	S3
2. General ATRP Procedure .....	S4
3. Conventional ATRP and (AGET) ATRP Employing PMDETA as the Ligand.....	S5
4. First-Order Kinetic Plots.....	S6
5. Evolution of $M_n$ as a Function of Conversion for the Polymerizations by Different Ligands.....	S8
6. NMR Spectra of the Polymers PAMA and PVMA.....	S10
7. The Concentration Effect on the (AGET) ATRP of MMA.....	S12
8. Evolution of $M_n$ as a Function of Conversion for the Polymerizations by <b>L4d</b> .....	S13
9. FTIR Spectra of the Polymers PAMA and PVMA .....	S14
10. $^1\text{H}$ NMR Spectra of the Copolymers.....	S15
11. The Spectra of PAMA and PVMA with Low Polymerization Degree.....	S18
12. Supplementary References.....	S21

## 1. General Information

Unless stated otherwise, all manipulations with air and moisture sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, or in an inert gas (N<sub>2</sub>)-filled glovebox. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. All the monomers were purchased and dried over activated CaH<sub>2</sub> overnight, followed by vacuum distillation and stored in bottles at -30 °C inside of a freezer. <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 400 MHz or Agilent Mercury 400 MHz spectrometer in chloroform-d. All signals were reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The number-average molecular weight ( $M_n$ ) and polydispersity index ( $\mathcal{D}$ ) were measured by gel permeation chromatography (GPC). GPC was performed on a Waters (USA) 1515 gel permeation chromatograph equipped with a Waters 2414 refractive-index detector with three commercial columns (Waters Styragel) connected in series. The analysis was undertaken at 25 °C with purified high-performance-liquid-chromatography-grade THF as the eluent at a flow rate of 1 mL/min. Calibration was performed with standard PMMAs. MALDI-TOF MS was conducted using a Shimadzu Axima Performance MALDI-TOF/TOF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion TOF detection performed using an accelerating voltage of 20 kV. Solutions in tetrahydrofuran (50  $\mu$ L) of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB) as a matrix (saturated solution), sodium iodide as the cationization agent (1.0 mg mL<sup>-1</sup>) and sample (1.0 mg mL<sup>-1</sup>) were mixed, and 0.7  $\mu$ L of the mixture was applied to the target plate.

## 2. General ATRP Procedure

All polymerizations were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of  $\text{CuBr}_2$ , ligand and  $\text{Cu}(0)$  powder in solvent was stirred at room temperature for 2 h under the atmosphere of nitrogen. After that, monomer and initiator were added into the ampule. The ampules were placed at room temperature. After stirring for the allotted period of time, an aliquot (0.1 mL) was removed and quenched with  $\text{CDCl}_3$  (0.5 mL). Conversion was determined by integration of the monomer vs. polymer backbone resonances in the  $^1\text{H}$  NMR spectrum of the crude product. After completion of the reaction, the contents of the ampules were dissolved in THF or  $\text{CH}_2\text{Cl}_2$ . The reaction was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 5 mL THF or  $\text{CH}_2\text{Cl}_2$ . This solution was added to an approximately 50-fold excess of rapidly stirred methanol. The precipitate that formed was filtered and washed with methanol. The precipitate was dried to constant weight in a vacuum oven at room temperature and then the dried samples were stored in dark at  $-30\text{ }^\circ\text{C}$ .

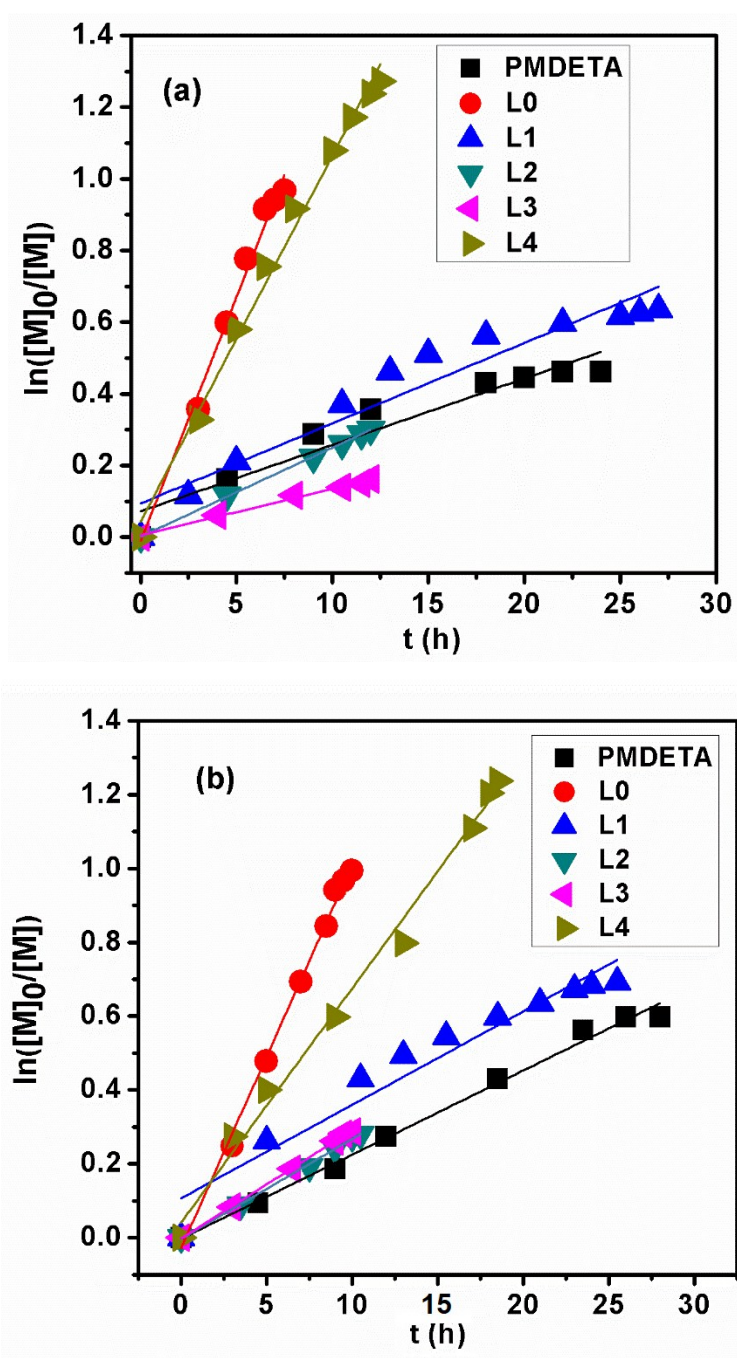
### 3. Conventional ATRP and (AGET) ATRP Employing PMDETA as the Ligand

**Supplementary Table S1. Conventional ATRP and (AGET) ATRP of Divinyl Monomers Employing PMDETA as the Ligand**

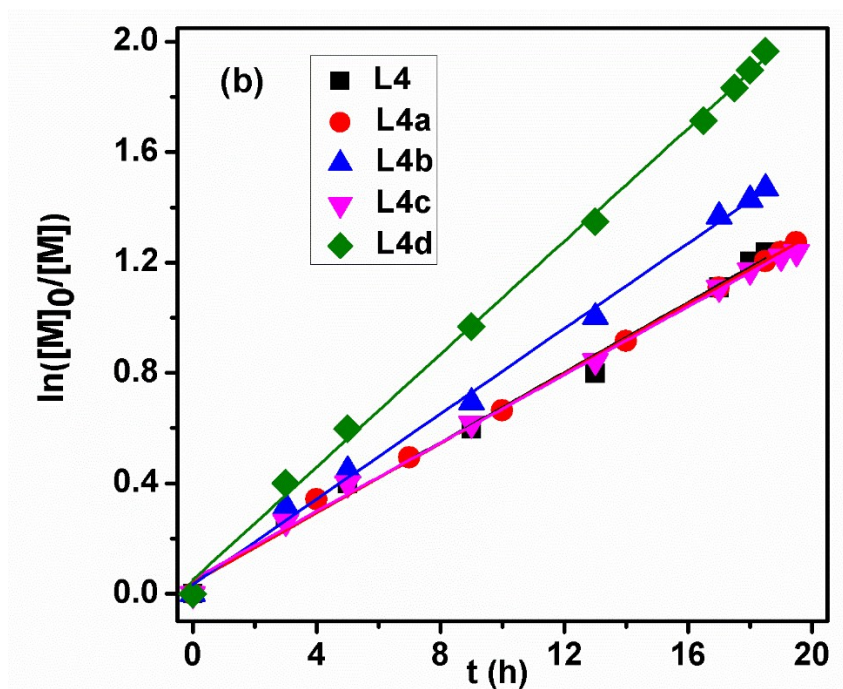
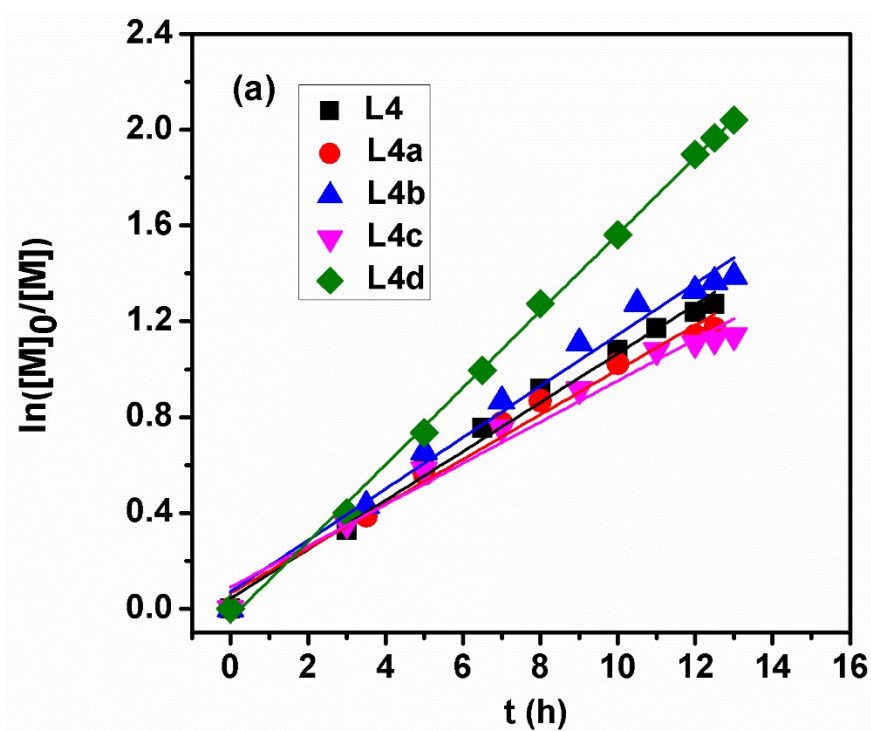
Run	Monomer	Conditions	Gel Point		Limit Conv. <sup>d</sup> (%)	$M_n^e$ ( $10^3$ )	$\mathcal{D}^e$	$M_{n,theory}$ ( $10^3$ )
			t (h)	Conv. <sup>c</sup> (%)				
1	AMA	conventional ATRP <sup>a</sup>	4.2	38 <sup>c</sup>	–	–	–	–
2	VMA	conventional ATRP <sup>a</sup>	0.5	17 <sup>c</sup>	–	–	–	–
3	AMA	(AGET) ATRP <sup>b</sup>	not detected		37 <sup>d</sup>	19.7	2.0	4.80
4	VMA	(AGET) ATRP <sup>b</sup>	not detected		45 <sup>d</sup>	21.3	2.3	5.18

<sup>a</sup> Conditions:  $n(M):n(EBIB):n(CuBr):n(PMDETA) = 100:1:1:1$ ,  $V_{Toluene} = V_{Monomer}$ , at 70 °C. <sup>b</sup> Conditions:  $n(M):n(BPN):n(CuBr_2):n(PMDETA):n(Cu(0)) = 200:2:1:2:4$ , 40 h, at 20 °C, THF was employed as the solvent,  $V_{THF} = V_{AMA}$ ,  $V_{THF} = 4V_{VMA}$ . <sup>c</sup> The monomer conversion at gel point, which is the monomer conversion when slight gelation just occurred and obtained on the monomer basis by <sup>1</sup>H NMR or weighing. <sup>d</sup> The highest monomer conversion during the whole polymerization measured by <sup>1</sup>H NMR. <sup>e</sup> Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PMMA standards,  $\mathcal{D} = M_w/M_n$ .

#### 4. First-Order Kinetic Plots

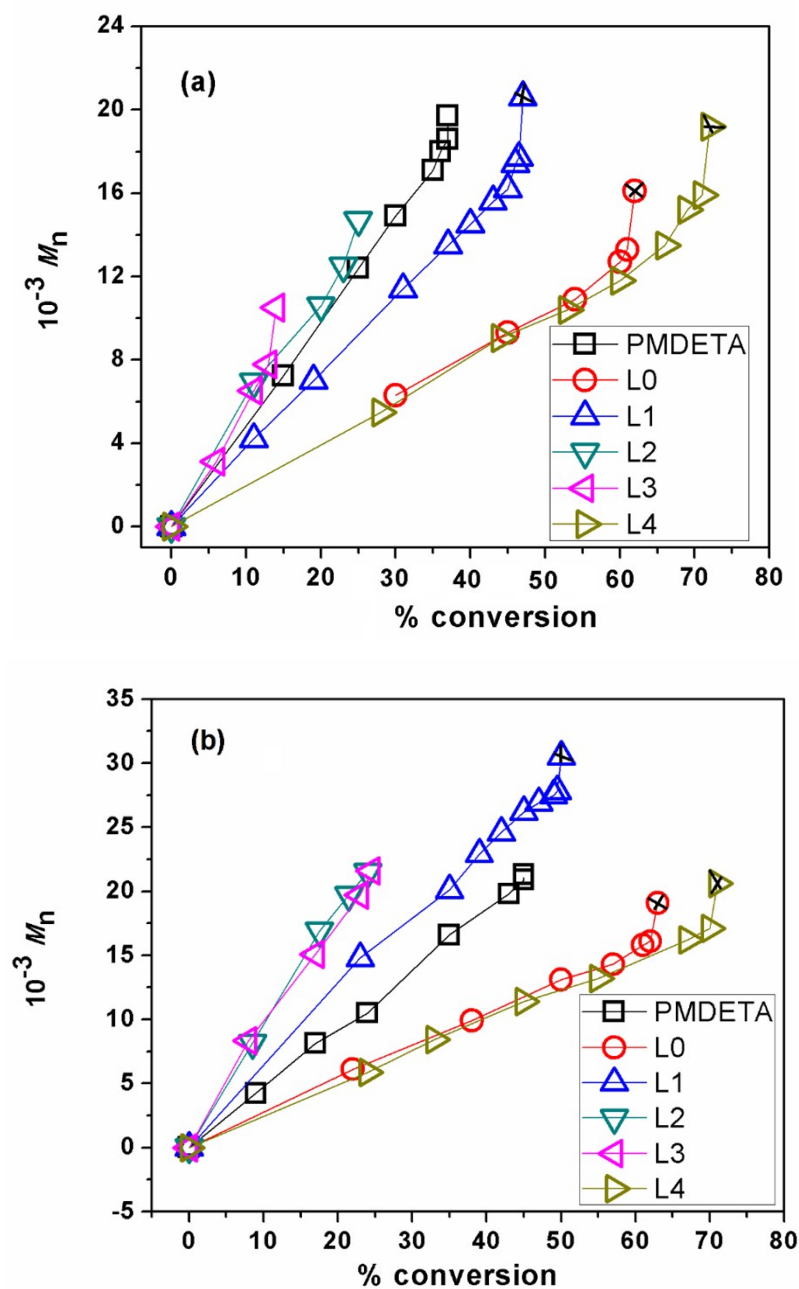


**Supplementary Figure S1.** First-order kinetic plot for ATRP of AMA (a) and VMA (b) employing ligands with different scaffolds under the conditions shown in Table 1.



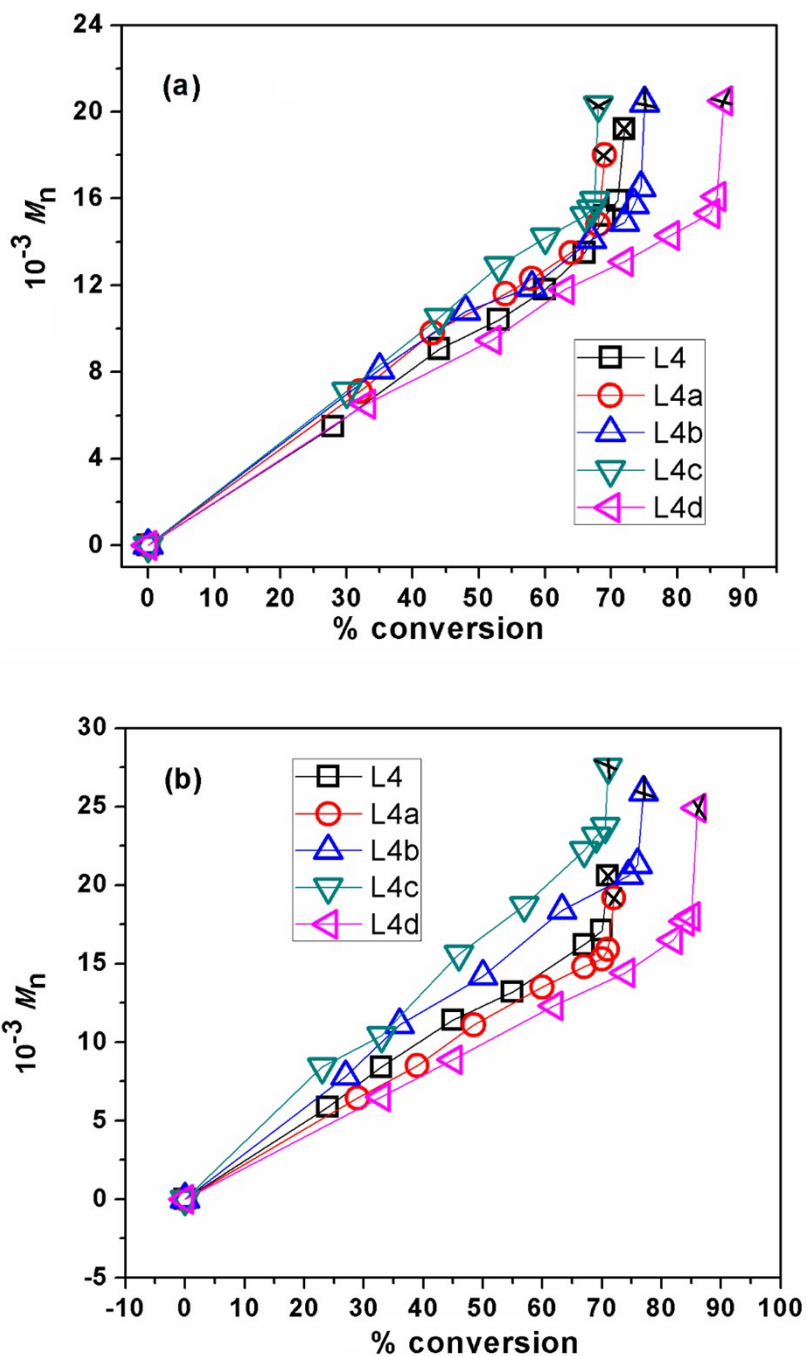
**Supplementary Figure S2.** First-order kinetic plot for ATRP of AMA (a) and VMA (b) employing ligands with different side arms under the conditions shown in Table 1.

## 5. Evolution of $M_n$ as a Function of Conversion for the Polymerizations by Different Ligands



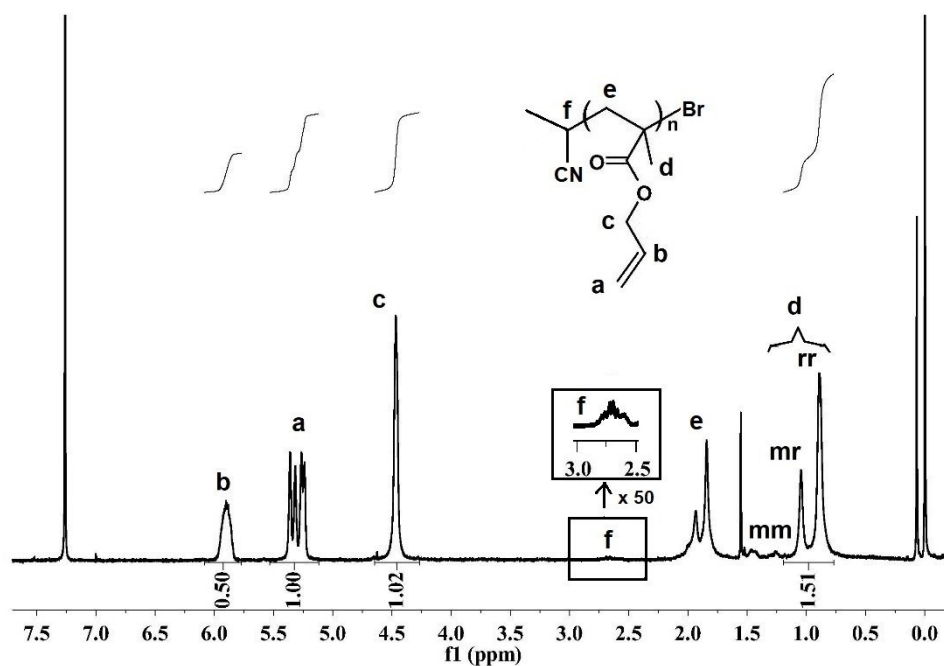
**Supplementary Figure S3.** Evolution of  $M_n$  (the soluble part) as a function of conversion for (AGET) ATRP of AMA (a) and VMA (b), employing ligands with different BOX scaffolds under the conditions shown in Table 1: the “x” in the signals means slight gelation just occurred. For the polymerizations by **L2** and **L3**, the molecular weights at gel point were not determined because of severe crosslinking during the pretreatment process of GPC measurement. For the polymerizations by **PMDETA**, no gelation was detected during the whole process.



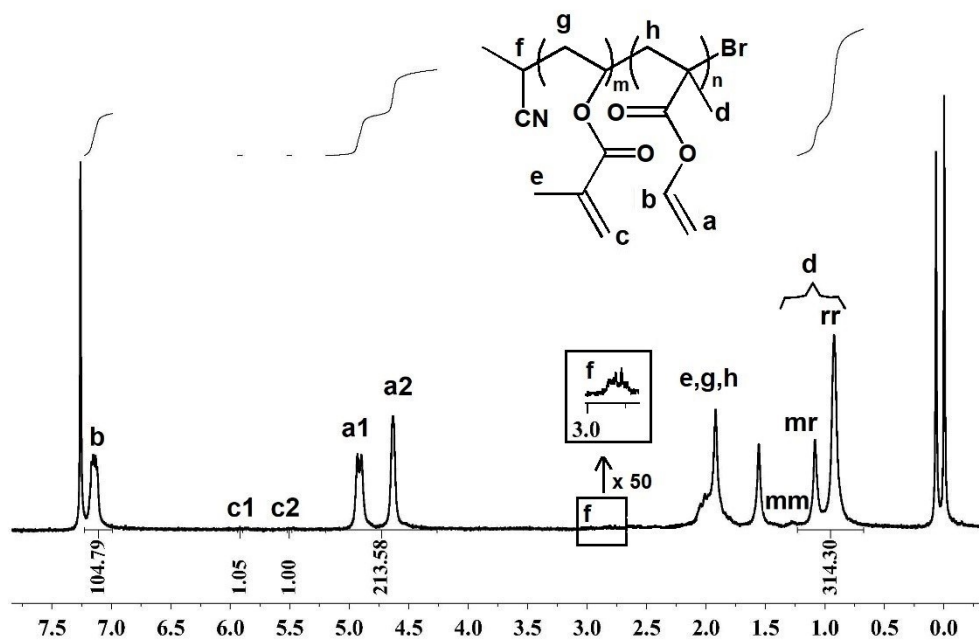


**Supplementary Figure S4.** Evolution of  $M_n$  (the soluble part) as a function of conversion for (AGET) ATRP of AMA (a) and VMA (b), employing indane-BOX ligands with different side arms under the conditions shown in Table 1: the “x” in the signals means slight gelation just occurred.

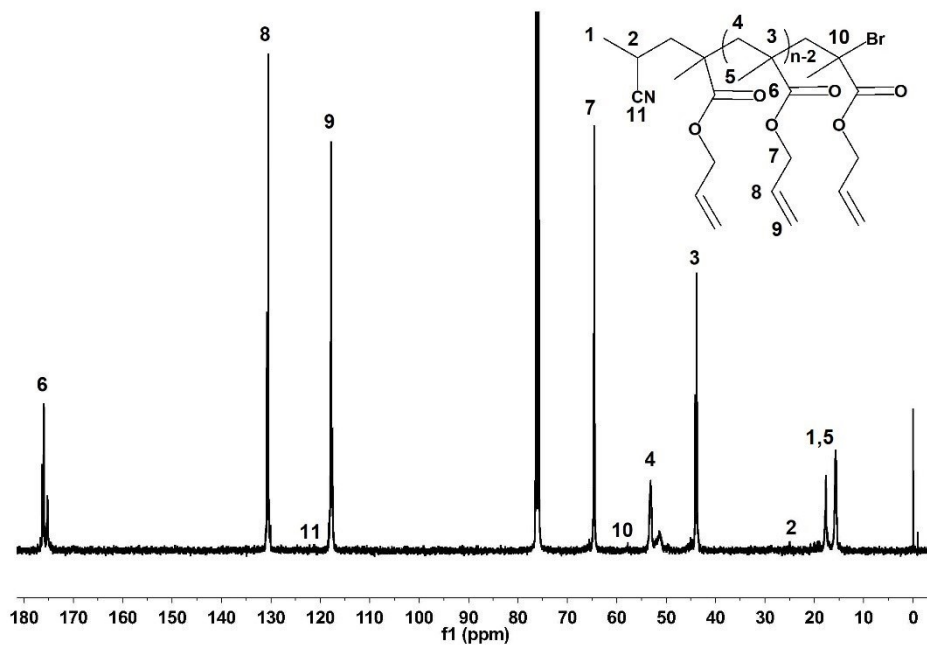
## 6. NMR Spectra of the Polymers PAMA and PVMA



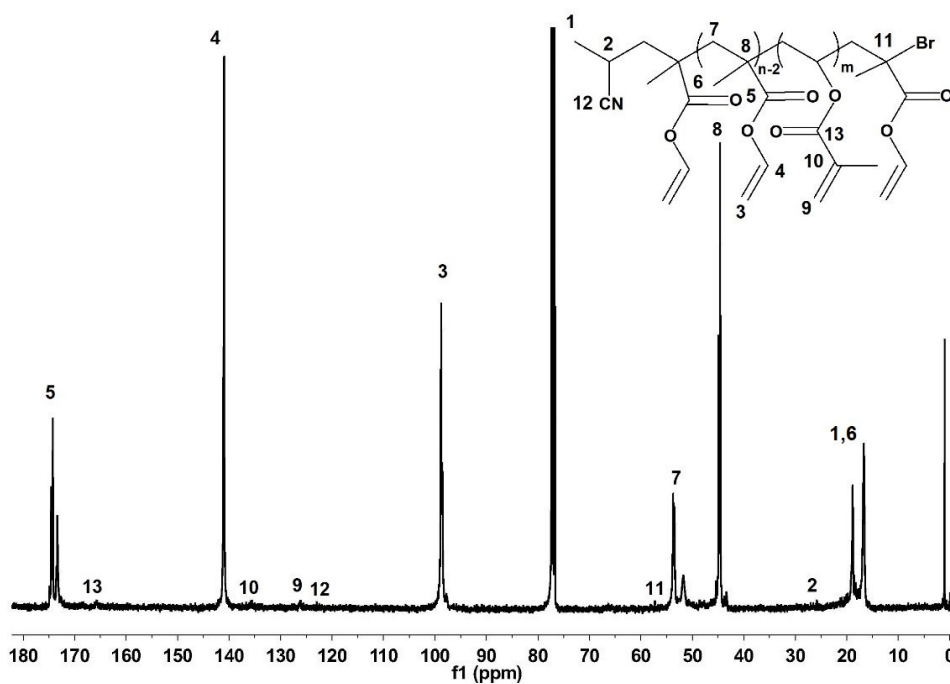
**Supplementary Figure S5.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PAMA (run 2 in Table 2).



**Supplementary Figure S6.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PVMA (run 5 in Table 2).



**Supplementary Figure S7.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C) spectrum of the polymer PAMA (run 2 in Table 2). The signals were assigned according to the literature.<sup>1</sup>



**Supplementary Figure S8.**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 25 °C) spectrum of the polymer PVMA (run 5 in Table 2). The signals were assigned according to the literature.<sup>1</sup>

## 7. The Concentration Effect on the (AGET) ATRP of MMA

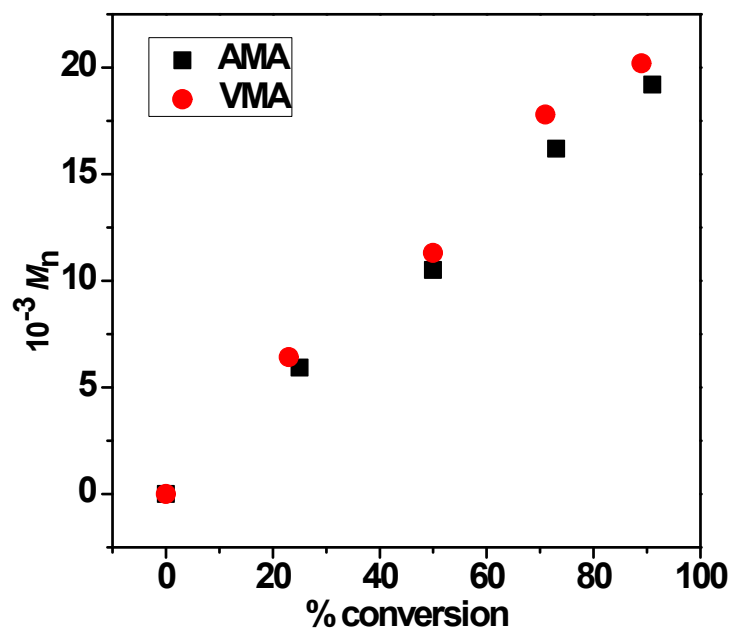
**Supplementary Table S2. (AGET) ATRP of MMA with Different Solvent Amount<sup>a</sup>**

Run	THF/MMA (V/V)	t (h)	Conv. <sup>b</sup> (%)	$M_{n, GPC}^c$ (10 <sup>3</sup> )	$\mathcal{D}^c$	$M_{n, theory}$ (10 <sup>3</sup> )
1	1/1	14	95	10.8	1.1	9.68
2	4/1	24	94	17.5	1.3	9.58
3	10/1	36	80	28.6	1.7	8.17

<sup>a</sup>Conditions:  $n(M):n(BPN):n(CuBr_2):n(L4d):n(Cu(0)) = 200:2:1:2:4$ , THF was employed as the solvent.

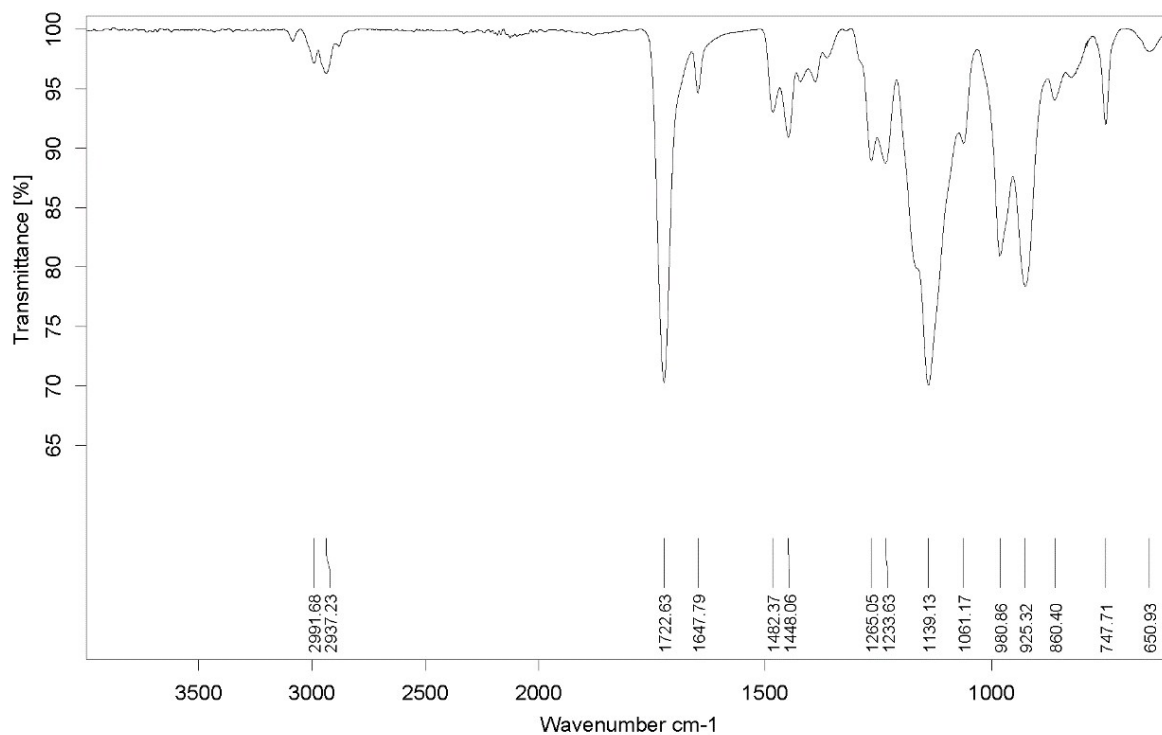
<sup>b</sup>Monomer conversion measured by <sup>1</sup>H NMR. <sup>c</sup>Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PMMA standards,  $\mathcal{D} = M_w/M_n$ .

## 8. Evolution of $M_n$ as a Function of Conversion for the Polymerizations by L4d

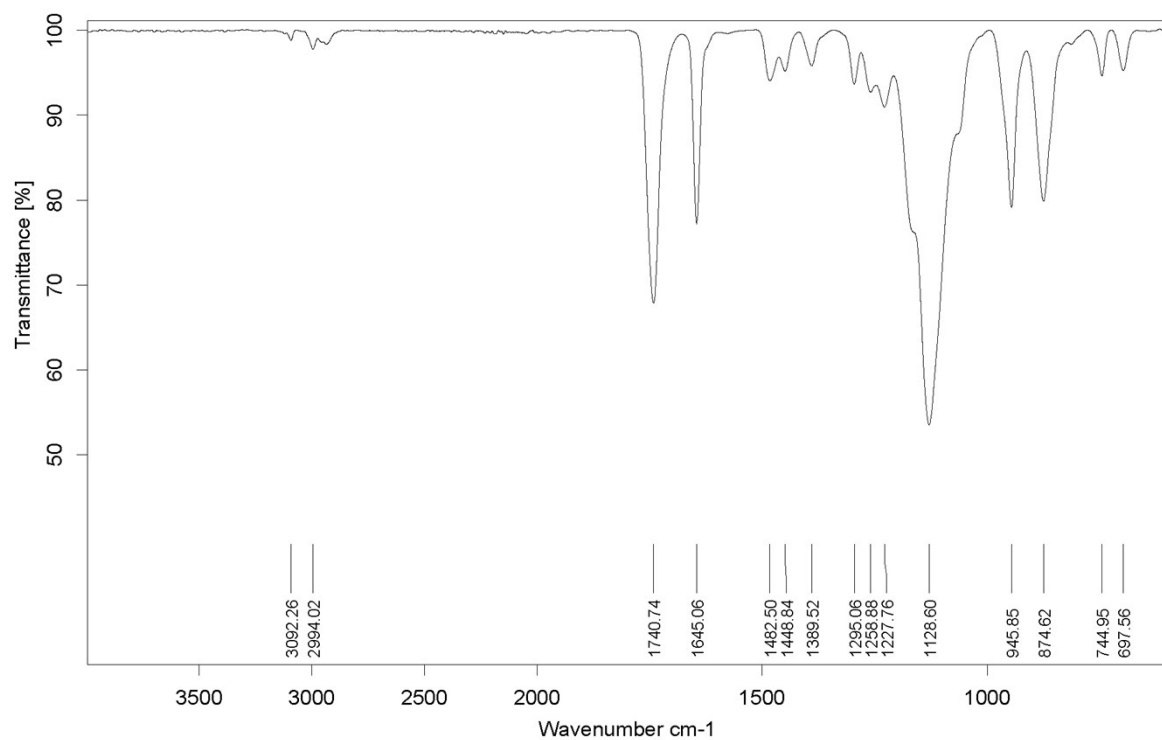


**Supplementary Figure S9.** Evolution of  $M_n$  as a function of conversion for (AGET) ATRP of AMA and VMA employing **L4d** as the ligand at 20 °C, respectively (runs 2 and 5 in Table 2).

## 9. FTIR Spectra of the Polymers PAMA and PVMA

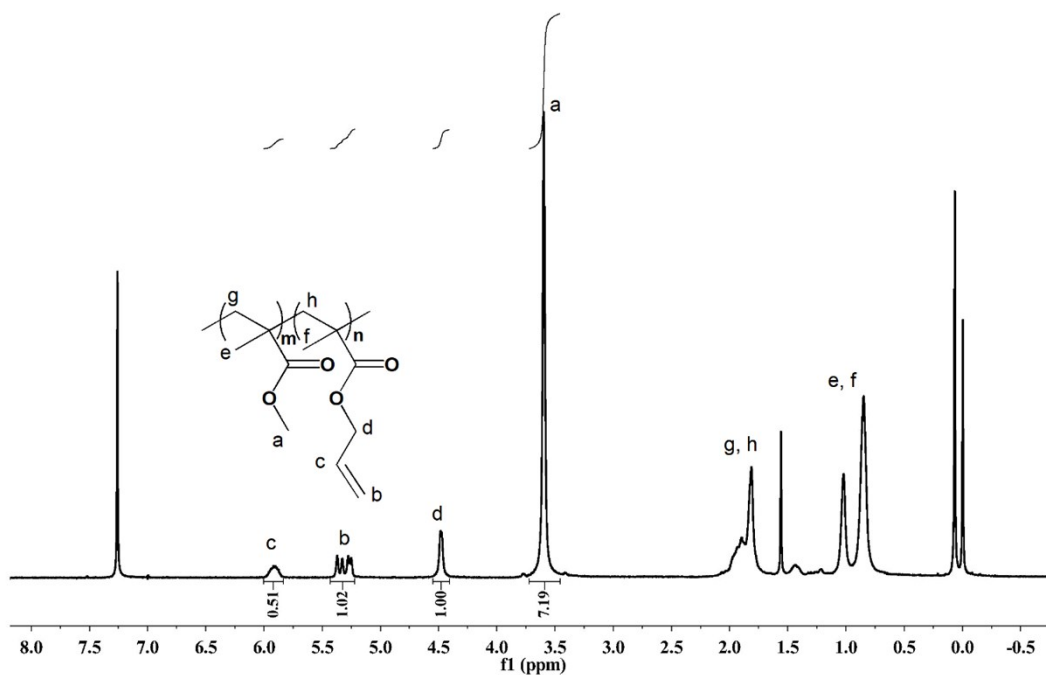


Supplementary Figure S10. FTIR spectrum of the polymer PAMA (run 2 in Table 2).

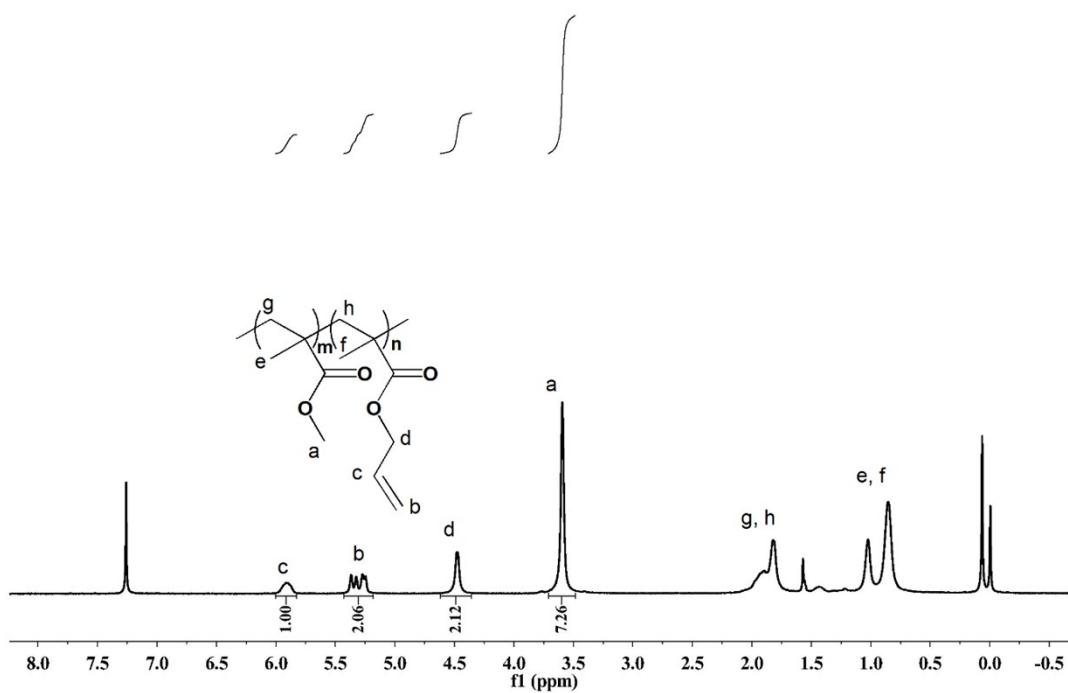


Supplementary Figure S11. FTIR spectrum of the polymer PVMA (run 5 in Table 2).

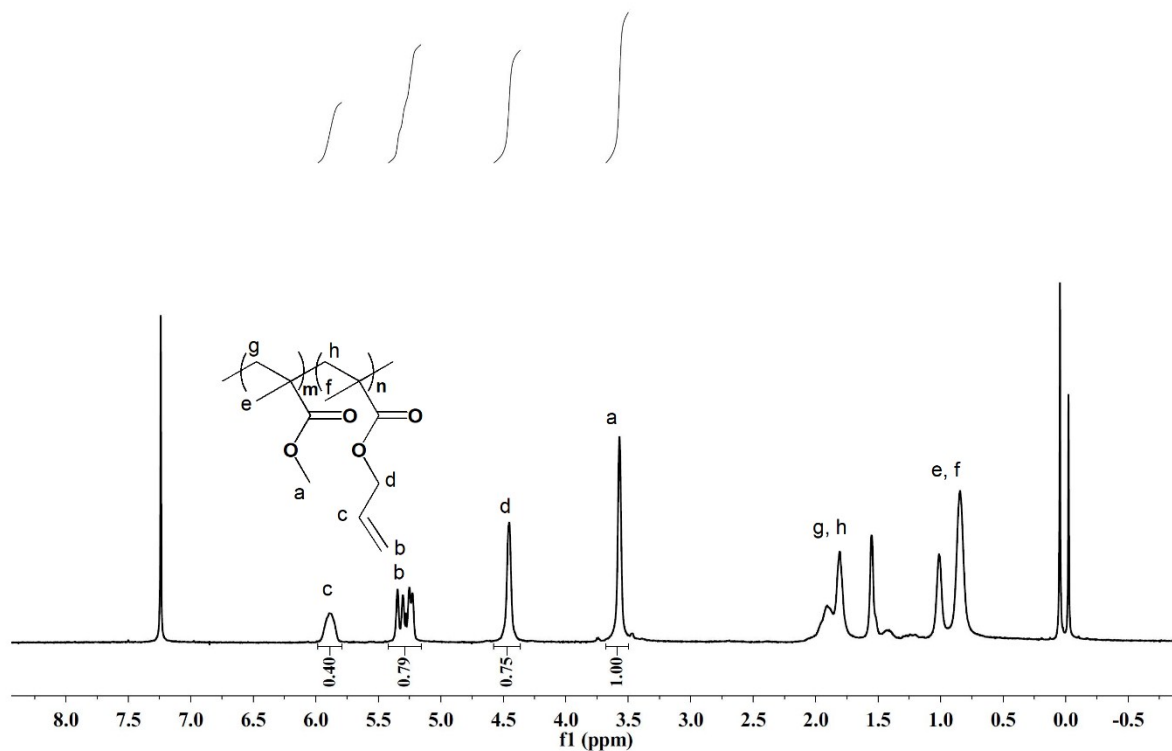
## 10. $^1\text{H}$ NMR Spectra of the Copolymers



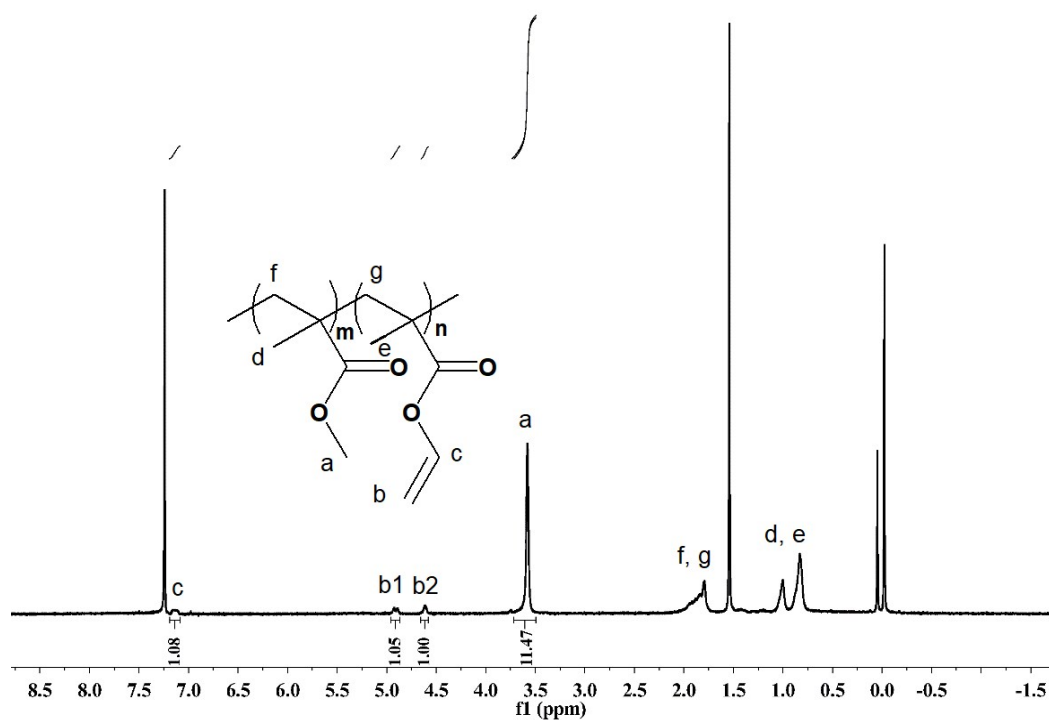
**Supplementary Figure S12.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum of poly-(MMA-*co*-AMA) (AMA unit content = 17 mol%, Run 1, Table 3).



**Supplementary Figure S13.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ) spectrum of poly-(MMA-*co*-AMA) (AMA unit content = 30 mol%, Run 2, Table 3).

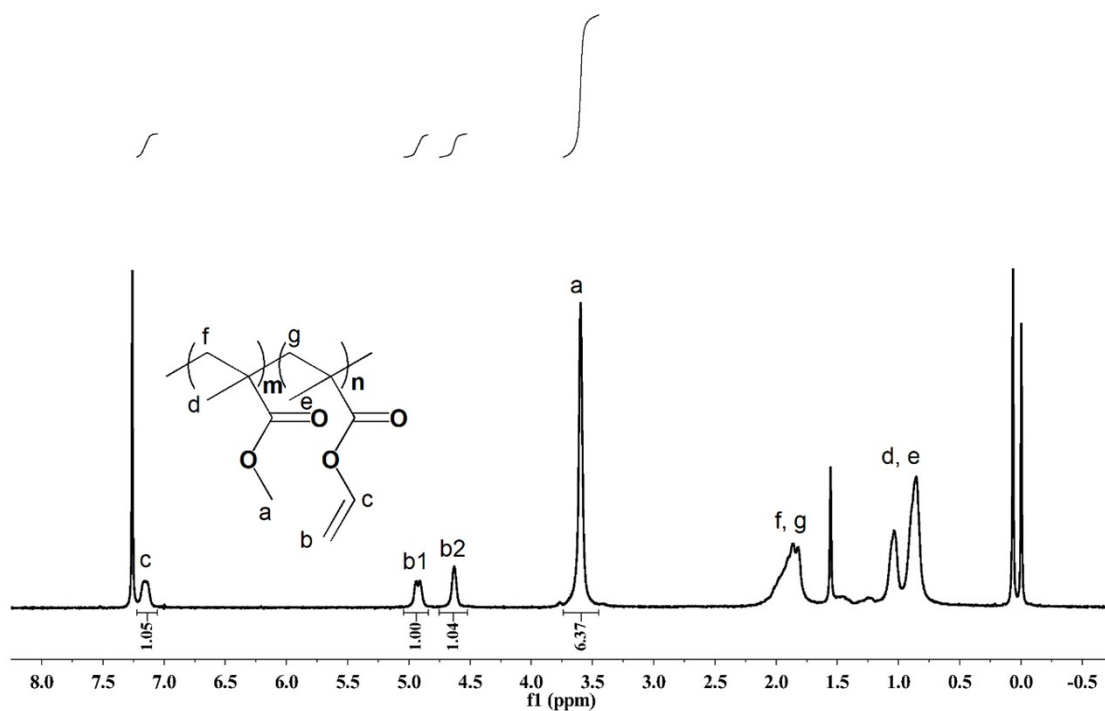


**Supplementary Figure S14.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) spectrum of poly-(MMA-co-AMA) (AMA unit content = 54 mol%, Run 3, Table 3).

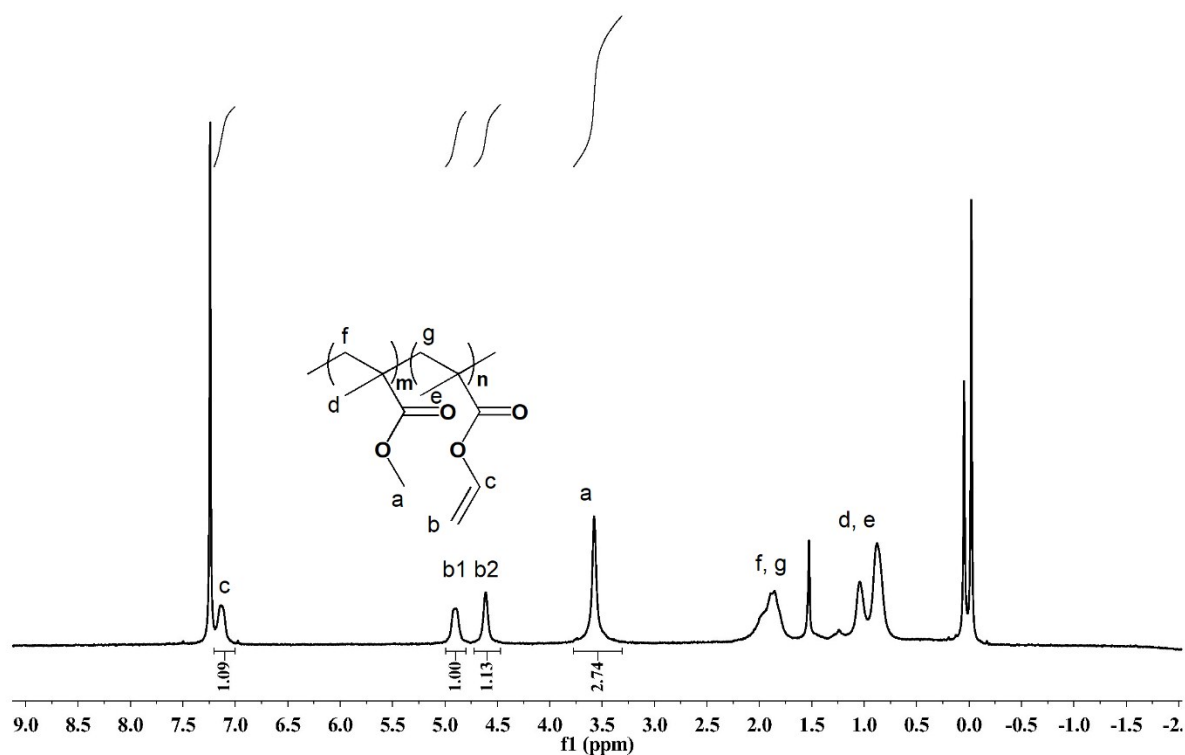


**Supplementary Figure S15.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) spectrum of poly-(MMA-co-VMA) (VMA unit content = 21 mol%, Run 4, Table 3).



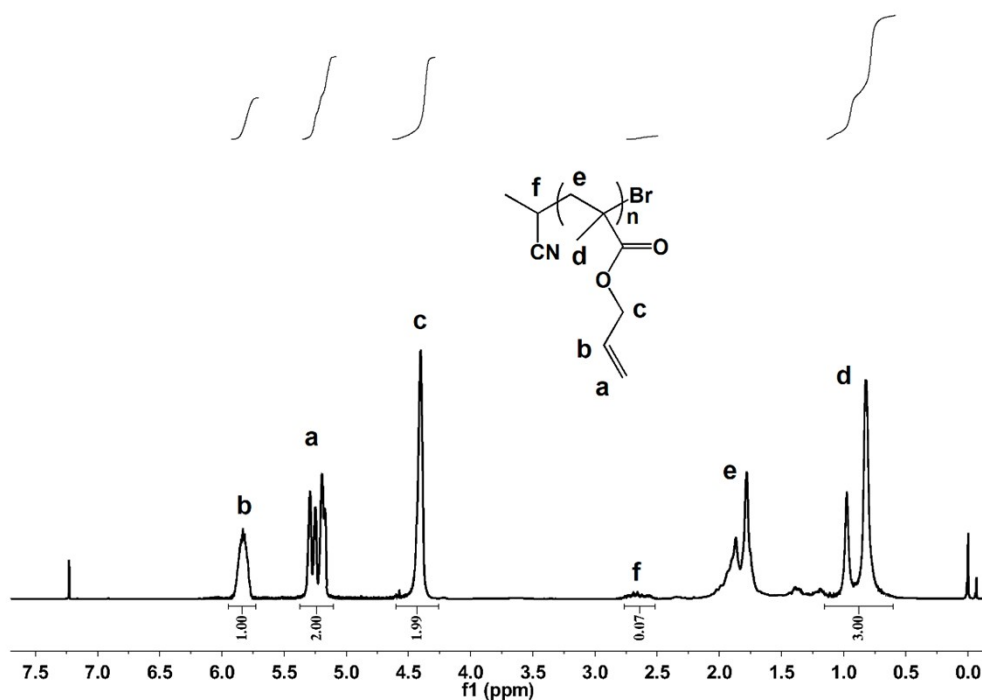


**Supplementary Figure S16.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) spectrum of poly-(MMA-co-VMA) (VMA unit content = 33 mol%, Run 5, Table 3).

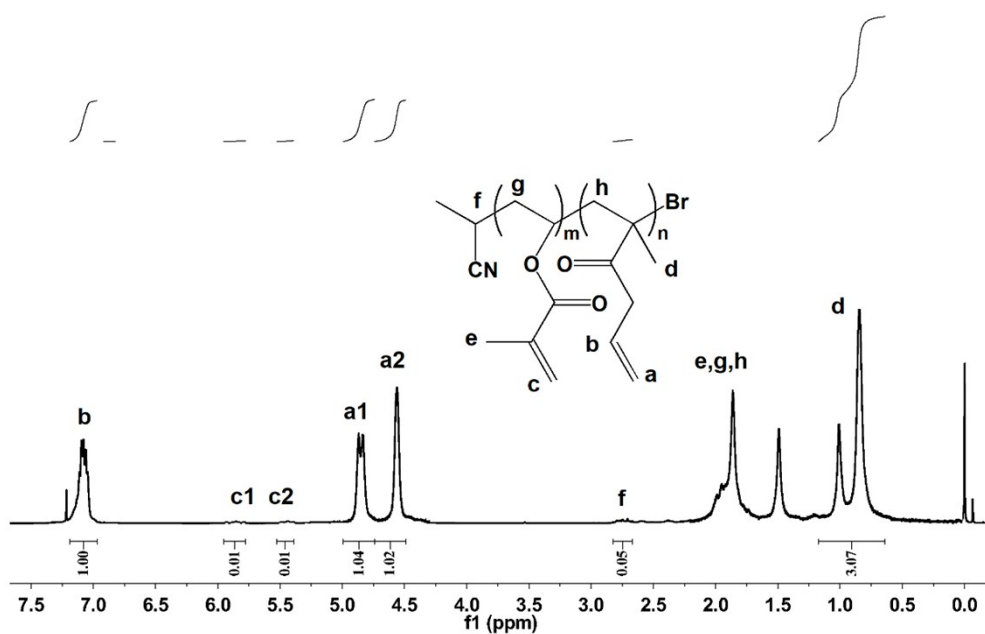


**Supplementary Figure S17.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25°C) spectrum of poly-(MMA-co-VMA) (VMA unit content = 54 mol%, Run 6, Table 3).

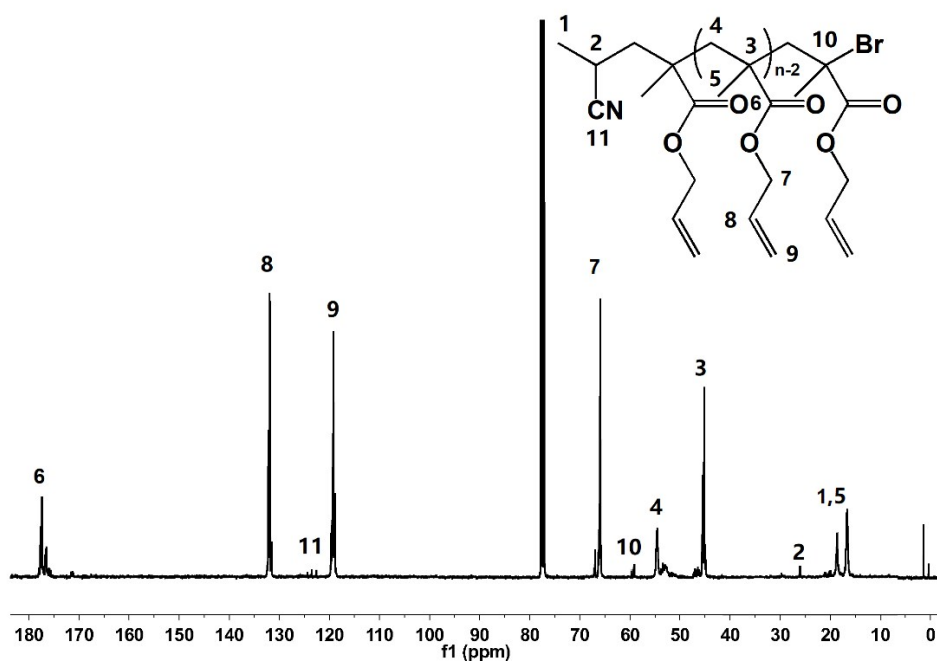
## 11. The Spectra of PAMA and PVMA with Low Polymerization Degree



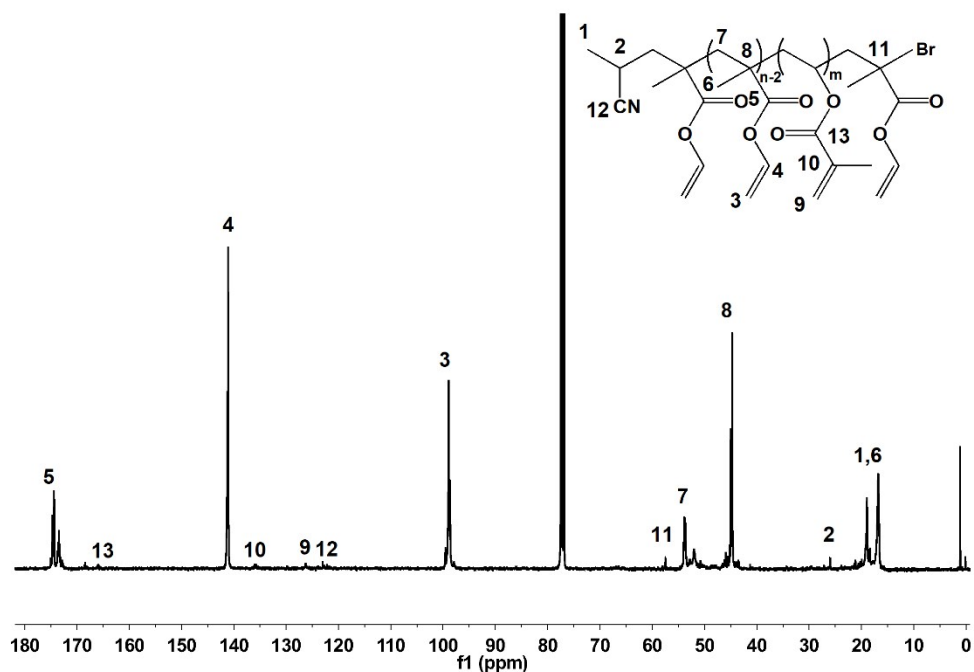
**Supplementary Figure S18.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PAMA ( $M_n = 2397$ ).



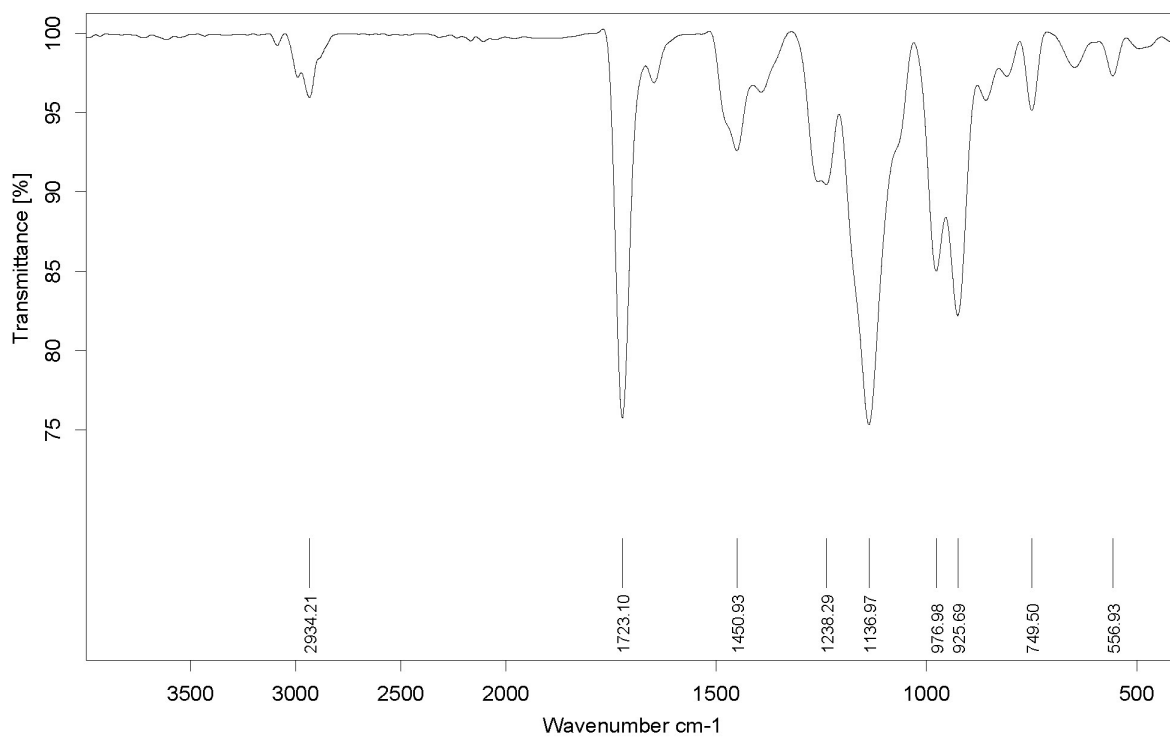
**Supplementary Figure S19.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PVMA ( $M_n = 2272$ ).



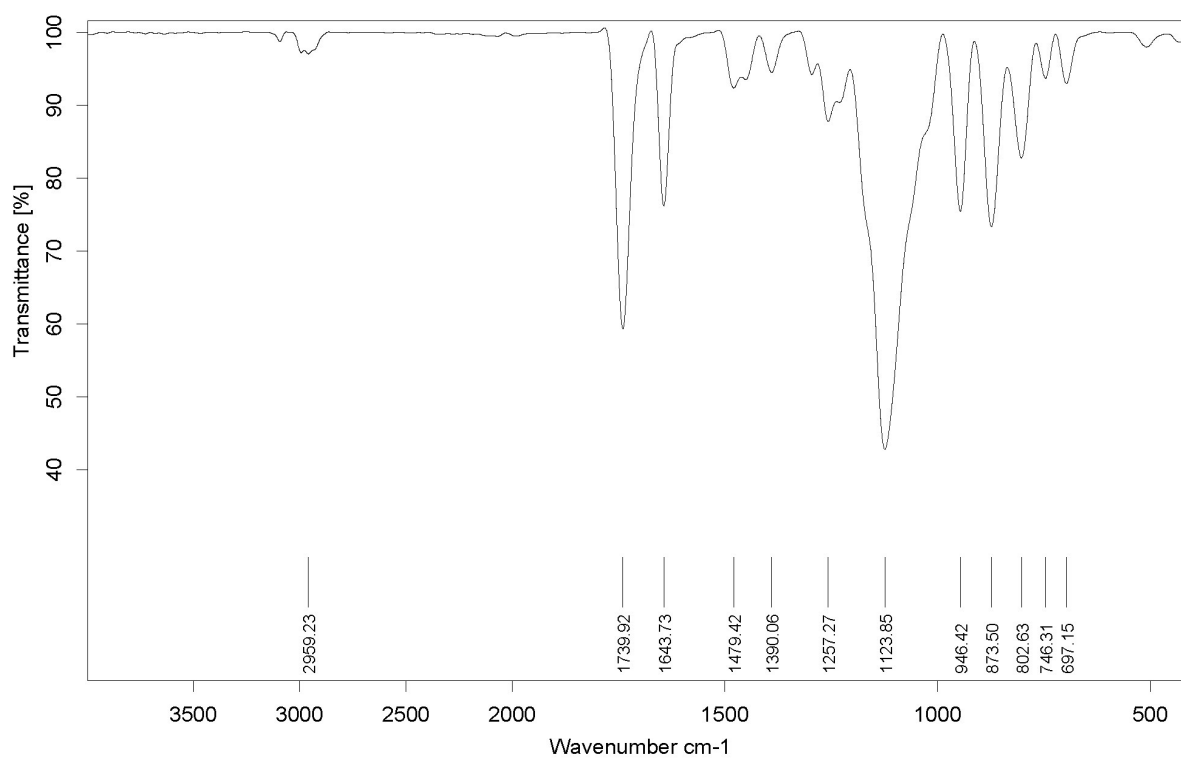
**Supplementary Figure S20.** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PAMA ( $M_n = 2397$ ).



**Supplementary Figure S21.** <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C) spectrum of the polymer PVMA ( $M_n = 2272$ ).



**Supplementary Figure S22.** FTIR spectrum of the polymer PAMA ( $M_n = 2397$ ).



**Supplementary Figure S23.** FTIR spectrum of the polymer PVMA ( $M_n = 2272$ ).

## 12. Supplementary References

1. París, R., de la Fuente, J. L. Solvent effect on the atom transfer radical polymerization of allyl methacrylate. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6247–6261.