

# $\alpha$ -(Aminomethyl)acrylate: Polymerization and spontaneous post-polymerization modification of $\beta$ -amino acid ester for pH- / temperature- responsive material

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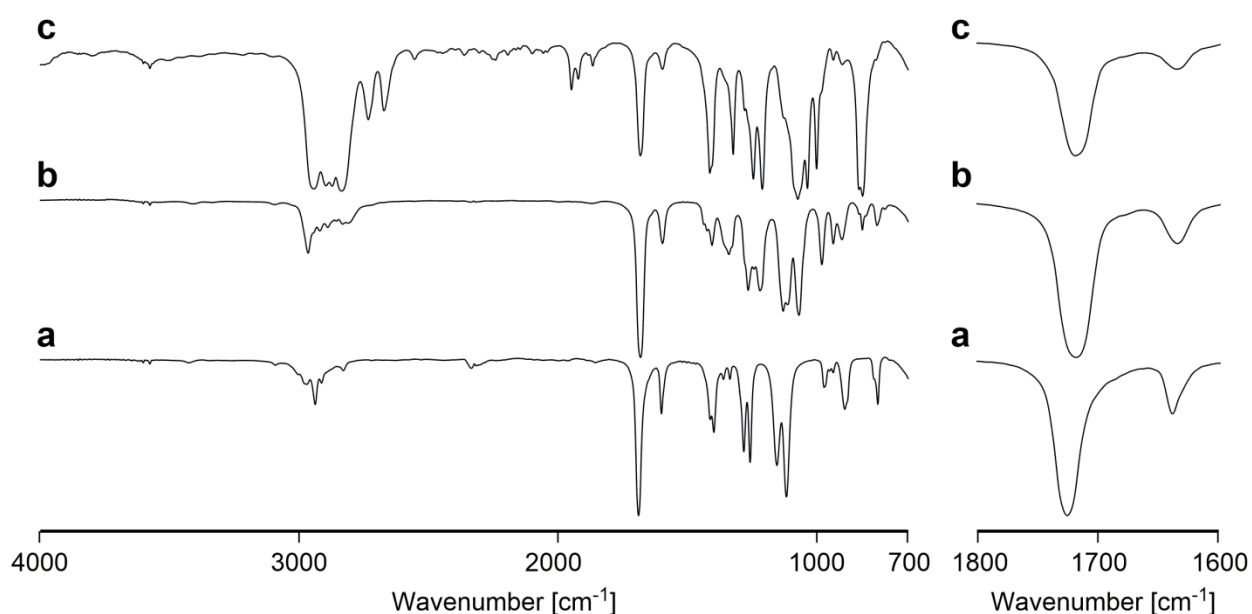
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## Supporting Information

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**Fig. S1.** IR absorption of **a**: methyl methacrylate (MMA), **b**: **2b** and **c**: **2b** in 1,4-dioxane solution (1 M).

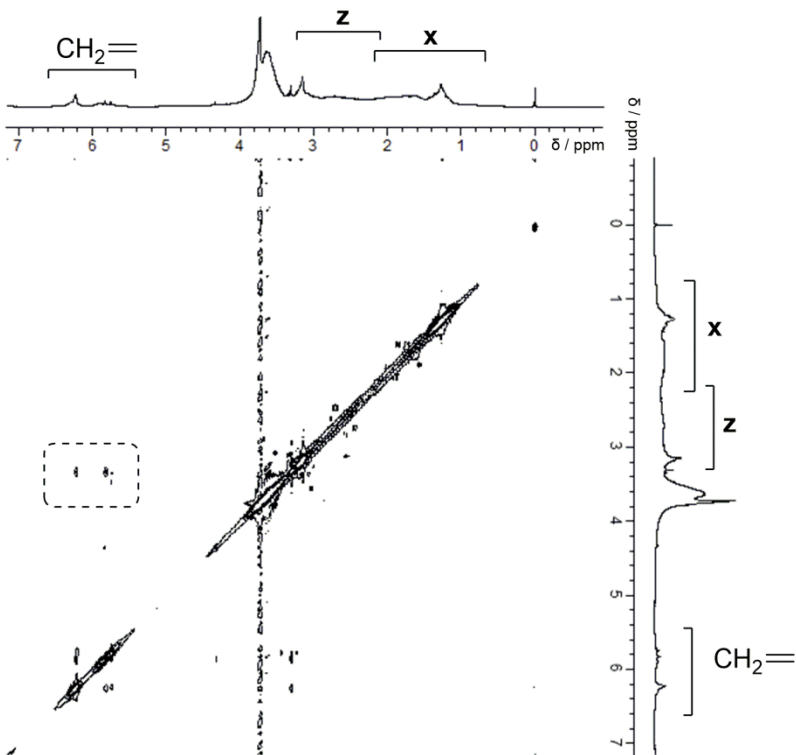


Fig. S2  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **poly(2a)**.

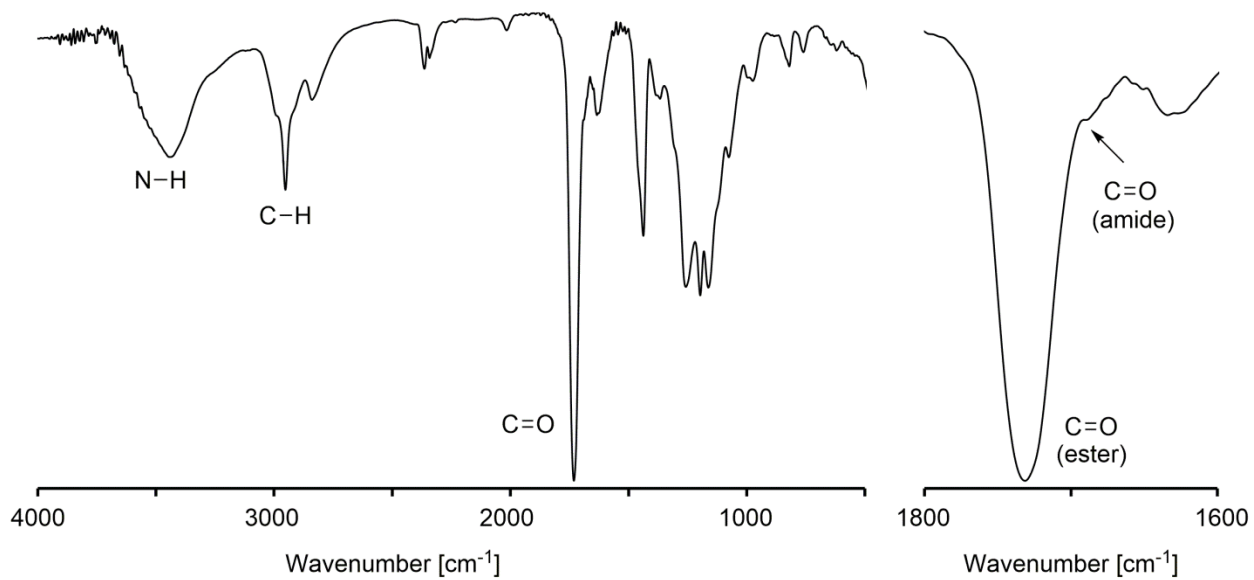


Fig. S3 IR spectrum of **poly(2a)**.

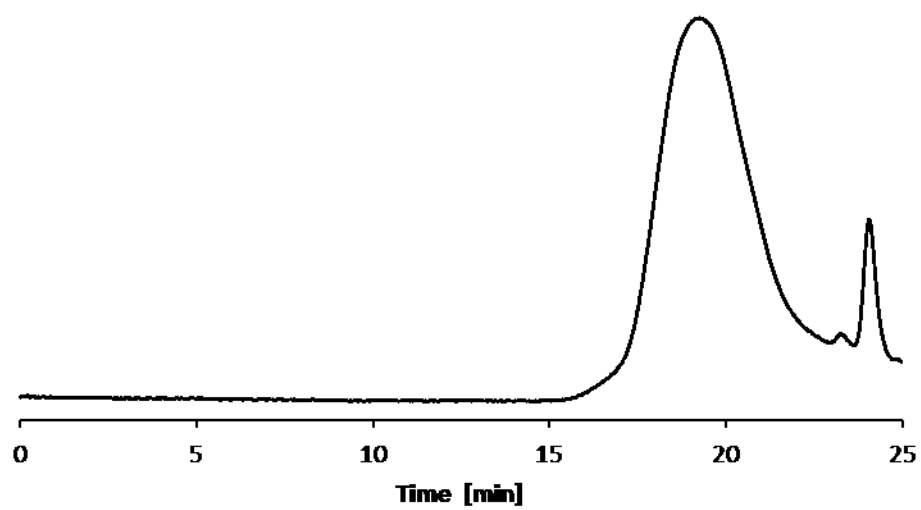
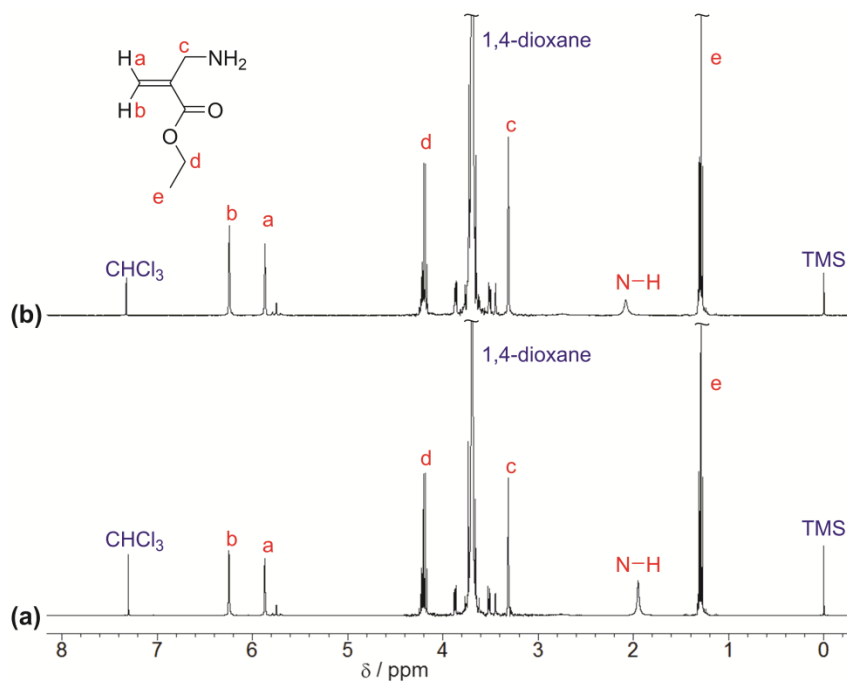


Fig. S4 SEC curve of poly(2b) (Run 3).

## Appendix

### 1. Thermal stability of **2b**.

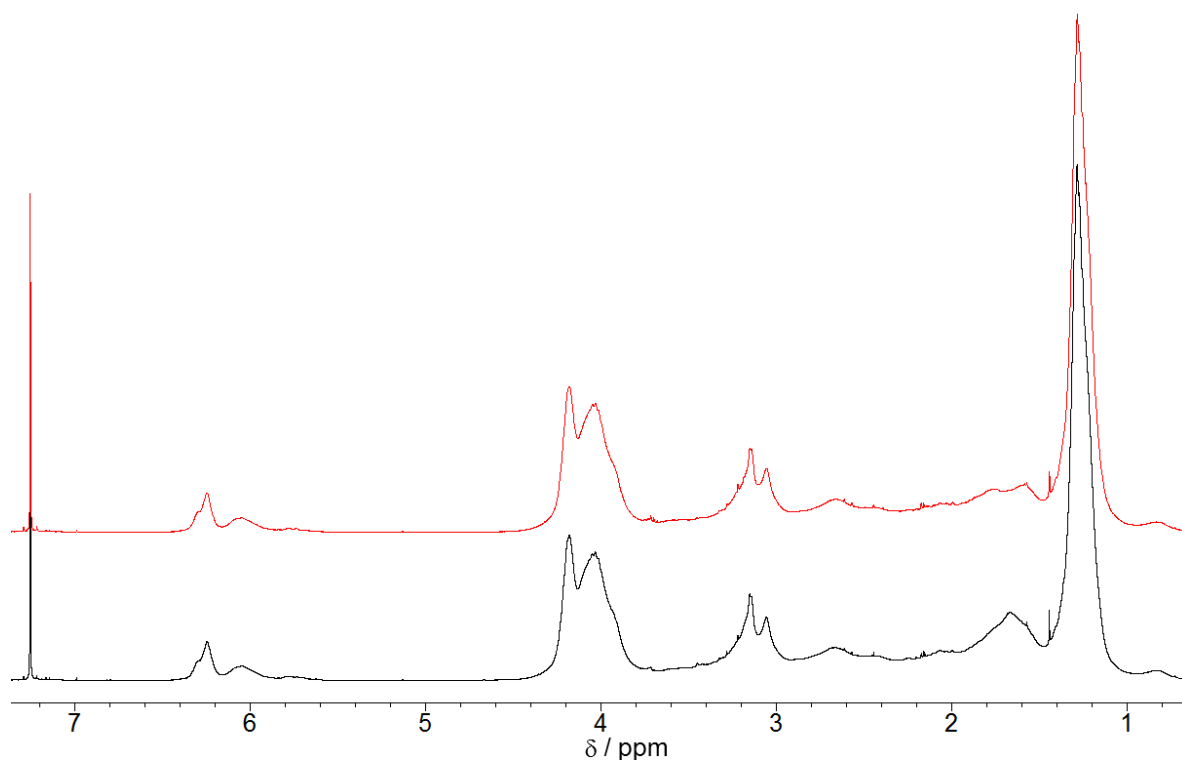
In order to remove the possibility of the ester-amide exchange between two monomeric molecules during polymerization, the thermal stability of monomer was investigated. A solution of **2b** (517 mg, 4.00 mmol) in 1,4-dioxane (2.0 mL) was heated at 60 °C for 12 h, and the small fraction of reaction mixtures was sampled and dissolved in CDCl<sub>3</sub> (0.70 mL) to measure the <sup>1</sup>H NMR spectrum. No change was observed in <sup>1</sup>H NMR spectra before and after heating (Fig. S5). Thus, it was concluded that **2b** itself was so stable that it underwent no spontaneous reaction under this condition. As the polymerization was carried out under the same conditions, monomers might not have relation to the side-reaction, ester-amide exchange.



**Fig. S5.** <sup>1</sup>H NMR spectra of **2b** in 1,4-dioxane (a) before and (b) after heating at 60 °C (400 MHz, CDCl<sub>3</sub>, 30 °C).

## 2. Thermal stability of poly(2b).

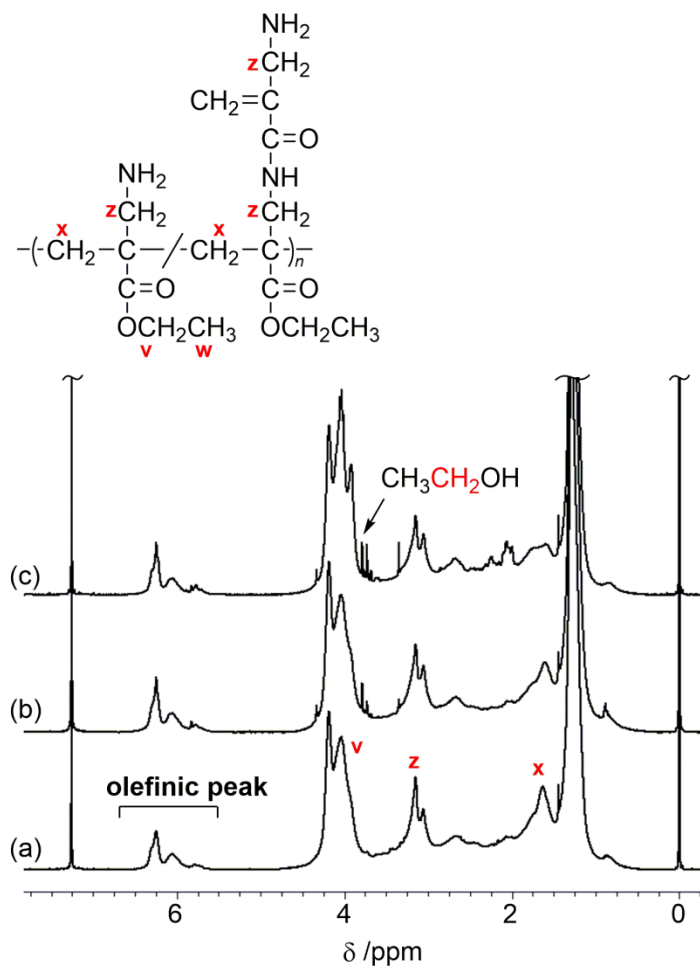
In order to remove the possibility of the ester-amide exchange between two polymeric molecules, the thermal stability of polymer was investigated. A solution of **poly(2b)** (20 mg) in  $\text{CDCl}_3$  (0.7 mL) was heated at 60 °C for 24 h, and the  $^1\text{H}$  NMR spectrum was observed. No change was found in  $^1\text{H}$  NMR spectra before and after heating (Fig. S6). Thus, it was concluded that **poly(2b)** itself was so stable that it underwent no spontaneous reaction under this condition. As the polymerization was carried out under the same conditions, polymer alone might not undergo the ester-amide exchange.



**Fig. S6.**  $^1\text{H}$  NMR spectra of **poly(2b)** in  $\text{CDCl}_3$  (a) before and (b) after heating at 60 °C (400 MHz,  $\text{CDCl}_3$ , 55 °C).

### 3. Thermal stability of poly(2b) in the presence of 2b.

In order to remove the possibility of the ester-amide exchange reaction between the two polymeric chains to form a cross-linked polymer, the isolated **poly(2b)** (64 mg, 0.50 mmol / unit, obtained in Run 6) and **2b** (64 mg, 5.0 mmol) was dissolved in toluene (0.50 mL) and heated at 60 °C for 46 h. The reaction mixture was poured to hexane and the precipitate was collected. Similarly, the reactions were conducted with **poly(2b)** (64 mg, 0.50 mmol / unit) and **2b** (640 mg, 50 mmol) in toluene (1 mL). In the <sup>1</sup>H NMR spectra (Fig. S7), some changes including the appearance of ethanol signals were observed.



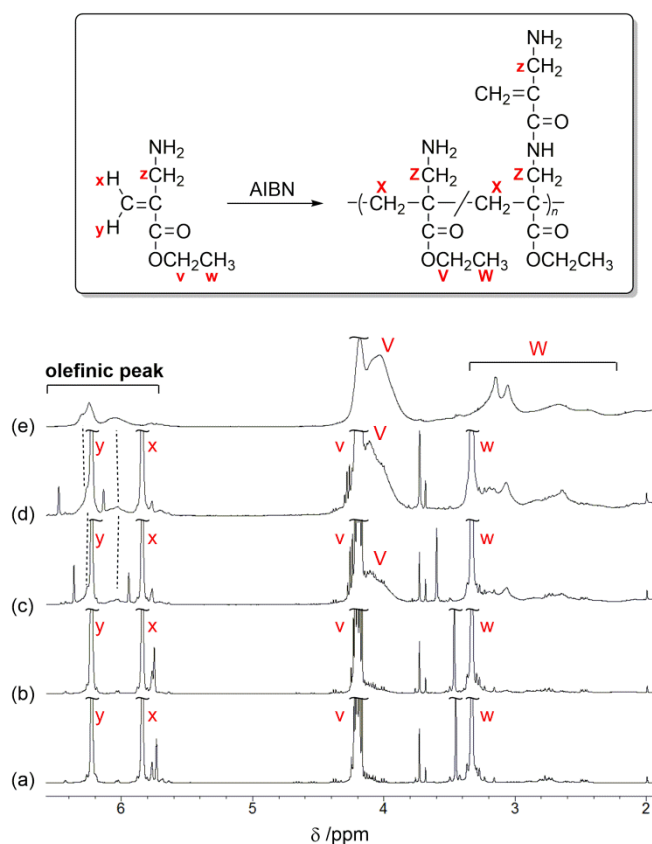
**Fig. S7.** <sup>1</sup>H NMR spectra of (a) **poly(2b)**, (b) a product of the reaction between **poly(2b)** and **2b** (1 : 1 per monomeric unit) heated at 60 °C for 46 h in 1,4-dioxane and (c) that of the reaction between **poly(2b)** and **2b** (1 : 10 per monomeric unit) (400 MHz, CDCl<sub>3</sub>, 55 °C).

#### 4. Monitoring of polymerization with NMR spectroscopy.

A solution of **2b** (155 mg, 1.20 mmol) and AIBN (9.84 mg, 60.0  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (2.10 mL) was degassed by freeze-pump-thaw cycles three times, and 0.70 mL of the reaction mixture was sampled into a NMR tube to monitor the polymerization with  $^1\text{H}$  NMR spectroscopy. The reaction mixture was heated at  $55^\circ\text{C}$  in NMR probe for 12 h, and  $^1\text{H}$  NMR spectra were recorded every 50 minutes.

Fig. S8 shows a partial series of the recorded  $^1\text{H}$  NMR spectra and that of isolated **poly(2b)**. Signals assignable to **poly(2b)** such as peak C (around 4.0 ppm) and peak D (around 3.0 ppm) were clearly observed after 5 h (Fig. S8c) and became significant after 12 h (Fig. S8d), while the signal of the vinylidene and amidic protons marked peak x was also observed. These results strongly indicate that the side reaction, ester-amide exchange reaction between polymer chains and monomeric molecules spontaneously occurred during polymerization.

Radical polymerization of **poly(2b)** was also monitored by precipitation of the polymerization mixture after 30 min, 3 h, and 6 h (Table S1). The conversion of **poly(2b)** was too small to isolate the polymeric product after 30 min (Run S1), whereas polymerization for more than 3 h (Runs S2-S4) afforded polymers in enough amount for isolation. Figure S5 shows the  $^1\text{H}$  NMR spectra of isolated polymers. In any case, peak X as described above was observed. These results also supported the fact that ester-amide exchange reaction occurs during the polymerization.



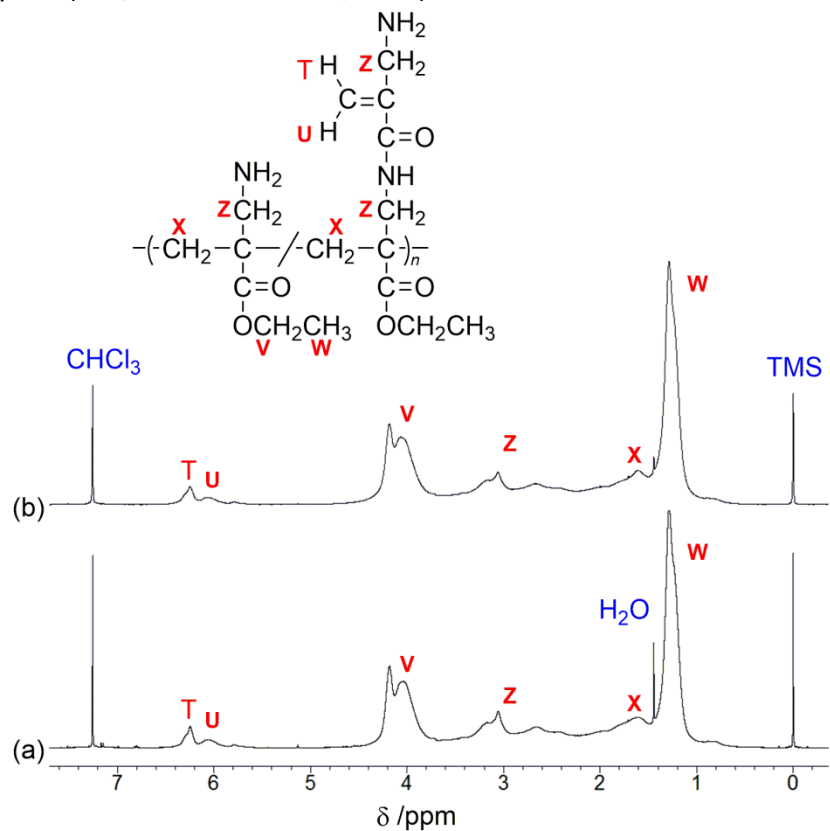
**Fig. S8.**  $^1\text{H}$  NMR spectra of polymerization mixture of **2b** after (a) 0h, (b) 1 h, (c) 5 h, and (d) 12 h and that of the isolated **poly(2b)** (400 MHz,  $\text{CDCl}_3$   $55^\circ\text{C}$ ).

**Table S1.** Radical polymerization of **2b** in 1,4-dioxane at 60 °C initiated by AIBN.

Run	Time / h	Conversion / % <sup>a</sup>	$M_n^b$	$M_w / M_n^b$
S1	0.5	5.1	-	-
S2	3.0	31.0	5000	2.40
S3	6.0	44.5	4000	2.86

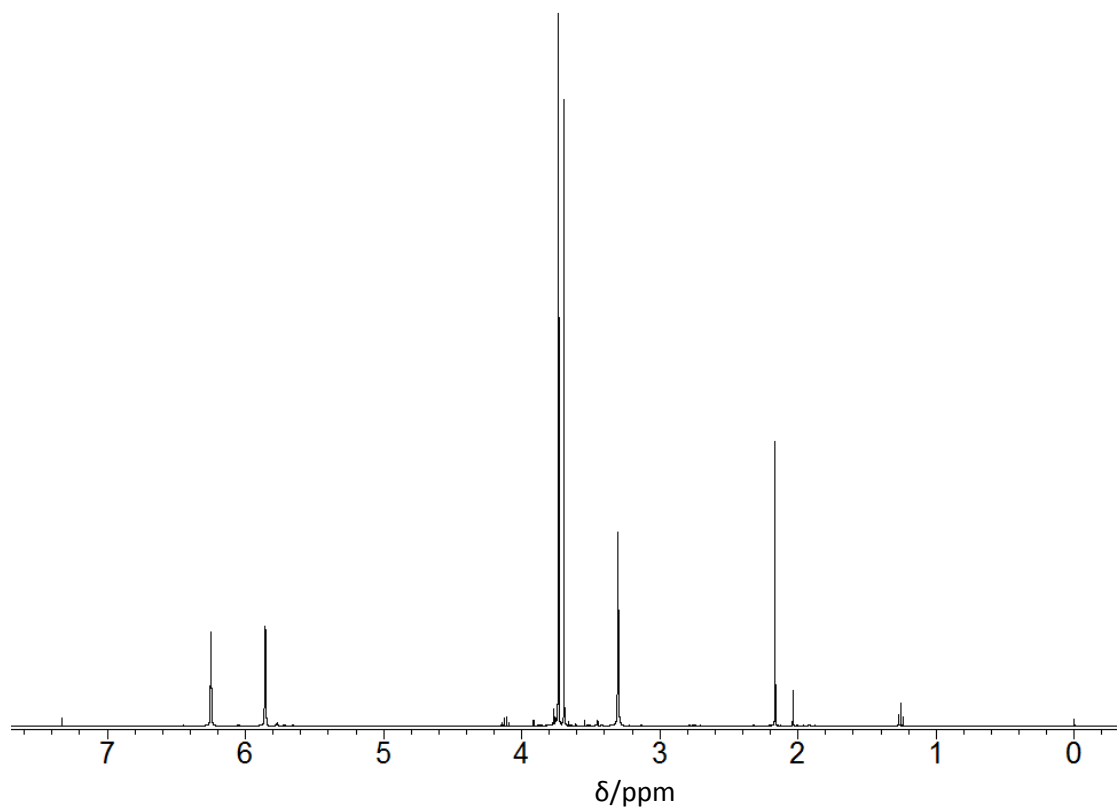
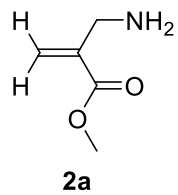
a) Determined by <sup>1</sup>H NMR spectroscopy (400 MHz, CDCl<sub>3</sub>, 30 °C).

b) Estimated by SEC (THF, PMMA standards, 40 °C).

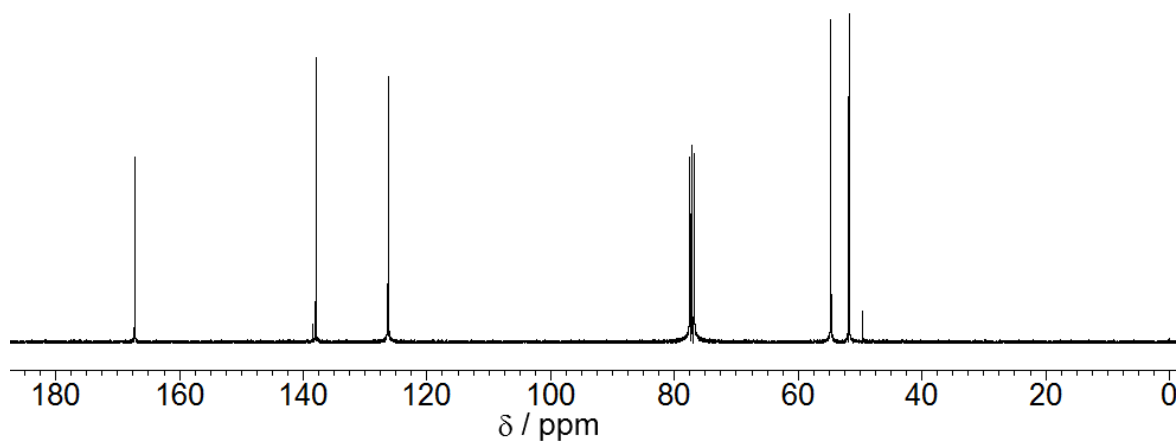
**Fig. S9.** <sup>1</sup>H NMR spectra of **poly(2b)** prepared by the polymerization for (a) 3 h and (b) 6 h (400 MHz, CDCl<sub>3</sub> 55 °C).



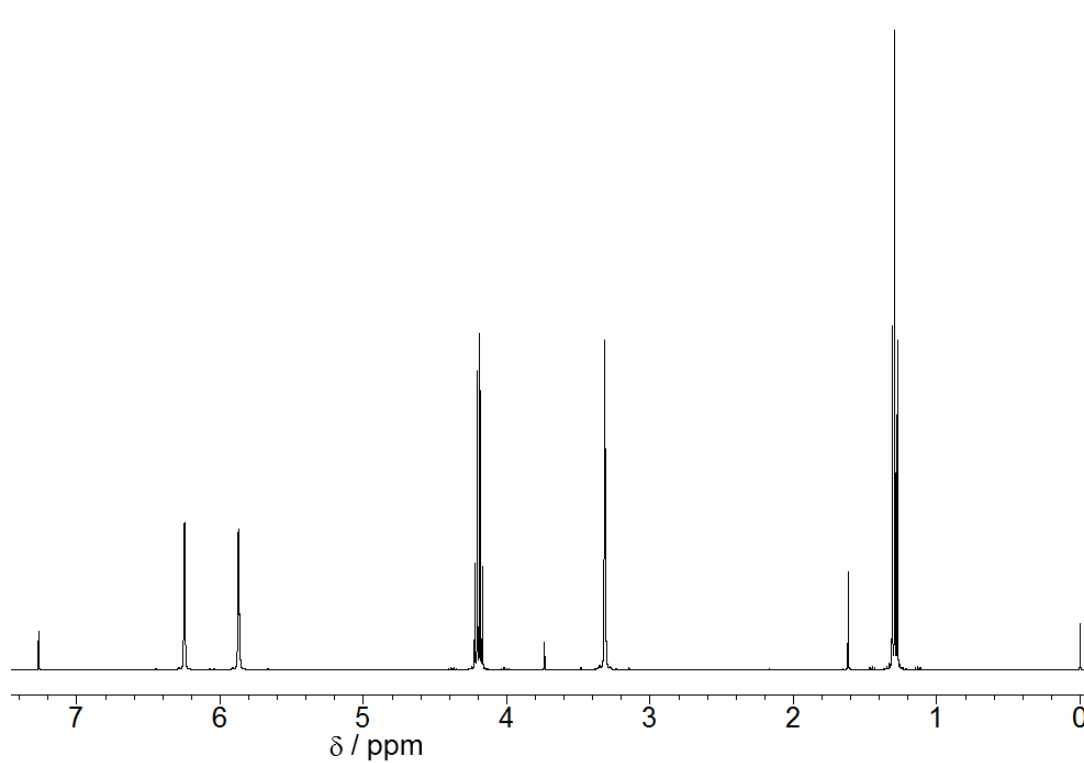
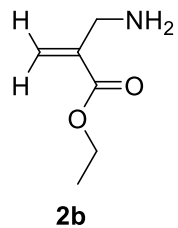
## 5. Spectral data of monomers.



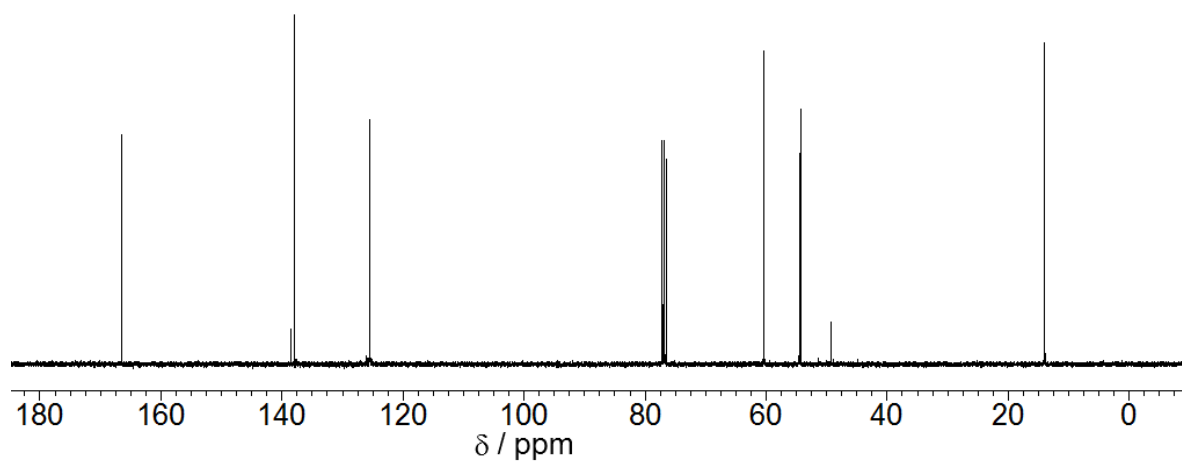
$^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 30 °C).



$^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 30 °C).



<sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 30 °C).



<sup>13</sup>C NMR spectrum (100 MHz, CDCl<sub>3</sub>, 30 °C).