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Effect of Amino Group Modification at Allyl Position of Methacrylamides on Polymerization and Polymer pH-/Thermo-Responsiveness

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Electronic Supplementary Information

EXPERIMENTS

Instruments

^{1}H NMR spectra were recorded in $CDCl_3$ (Across Organics) on AVANCE NEO (Bruker) and AVANCE III (Bruker) spectrometers. Chemical shifts in ^{1}H NMR spectra were referred to the signal of tetramethylsilane (TMS) and solvent ($CDCl_3$), respectively. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm _7.5 mm), Polymer Laboratories], using 0.5 wt% LiBr solution in *N*,*N*-dimethylformamide (DMF, Wako Pure Chemical Industries, for HPLC grade) as an eluent (flow rate = 0.8 mL min^{-1}), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (TSK-gel oligomer kit, Tosoh, M_n: 6.475×10^5, 2.522×10^5, 1.416×10^5, 2.912×10^4, 8.59×10^3, 4.25×10^3, 1.46×10^3, 8.30×10^2) and detected with UV (UV-4070, JASCO) and RI (RI-4030, JASCO) detectors. UV-vis spectra were recorded on V-400 (JASCO) and V-730 ST (JASCO) spectrometers equipped with temperature controller (ETCS-761).

Materials

tert-Butyl acrylate (**11**) was provided by Osaka Organic Chemical Industry Ltd. *N*-Isopropyl acrylamide was provided by KJ Chemicals Co. α-(Chloromethyl)acryloyl chloride (**13**) were prepared according to our previous reports.[1] Other chemicals were purchased from Tokyo Chemical Industry and Fujifilm Wako Pure Chemical Industry.

Monomer Synthesis

14a (Table 1, Entry 3)**:** **12** (0.684 g, 4.92 mmol) in $CHCl_3$ (98 mL) was added dropwise to a solution of *n*-propylamine (2.91 g, 49.8 mmol) in $CHCl_3$ (25 mL) over 100 min at −40 °C. The reaction mixture was stirred for 18 h. The reaction was quenched with water (300 mL). The separated organic layer was dried over $MgSO_4$, concentrated, and dried in *vacuo* to give **14a** (0.514 g, 56.7% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ/ppm 6.13 (d, *J*=2.02 Hz, 1H), 5.38 (m, 1H), 3.49 (d, *J* = 0.88 Hz, 2H), 3.29-3.21 (m, 2H), 2.58-2.55 (t, *J*=7.01 Hz, 2H), 1.60-1.46 (m, 4H), 0.96-0.84 (m, 6H).

14b was prepared in a similar manner to **14a**: ^{1}H NMR (400 MHz, CDCl$_3$, 25°C) δ/ppm 6.09 (d, *J* = 2.02 Hz, 1H), 5.37 (m, 1H), 4.05-4.15 (m, 1H), 3.47 (d, *J*=0.88, 2H), 2.76-2.86 (quin, *J* = 6.25 Hz, 1H), 1.18 (d, *J* = 6.57, 6H), 1.09 (d, *J* = 6.25, 6H)

14c was prepared in a similar manner to **14a**: ^{1}H NMR (400 MHz, CDCl$_3$, 26°C) δ/ppm 6.06 (d, *J*=2.02 Hz, 1H, a), 5.32 (m, 1H, b), 3.39 (d, *J*=0.69 Hz, 2H, c), 3.39 (s, 9H, e), 1.14 (s, 9H, d).

13a: **12** (3.64 g, 40.3 mmol) in CHCl$_3$ (5 mL) was added dropwise to a solution of *n*-propylamine (2.37 g, 40.0 mmol) and Et$_3$N (4.08 g, 40.3 mmol) in CHCl$_3$ (20 mL) over 100 min at −20 °C. The reaction mixture was stirred for 22 h. The reaction was washed with 10 wt% HCl aq (25 mL × 2) and brine (25 mL × 3). The separated organic layer was dried over MgSO$_4$ and concentrated. The residue was poured into Et$_2$O (70 mL) cooled at −20 °C. The precipitate was collected and dried in *vacuo* to give **13a** (1.73 g, 38.2% yield) as yellow oil.
^{1}H NMR (400 MHz, 25 °C, CDCl$_3$) : δ 6.30 (br, 1H, N*H*), 6.29 (d, *J* = 1.8 Hz, 0.33 H, C*H*=), 6.24 (d, *J* = 1.8 Hz, 0.67 H, C*H*=), 6.17 (d, *J* = 10.0 Hz, 0.67 H, C*H*=), 6.13 (d, *J* =10.0 Hz, 0.33 H, C*H*=), 5.60 (dd, *J1* = 10.0 Hz, *J2* = 1.8 Hz, 1H, C*H*=), 3.29 (q, *J* = 7.1 Hz, *N*-CH$_2$), 1.56 (q, *J* = 7.1 Hz, 2H, C*H$_2$*), 0.94 (t, J = 7.1 Hz, 3H, C*H$_3$*).

13b: **12** (1.12 g, 8.05 mmol) in CHCl$_3$ (80 mL) was added dropwise to a solution of isopropylamine (0.948 g, 16.0 mmol) in CHCl$_3$ (20 mL) over 100 min at −40 °C. The reaction mixture was stirred for 23 h. The reaction was washed with water (300 mL). The separated organic layer was dried over MgSO$_4$, concentrated and dried in *vacuo* to give **13b** (0.821 g, 63.1% yield) as white powder.
^{1}H NMR (400 MHz, 25 °C, CDCl$_3$) : δ 6.30 (br, 1H, N*H*), 5.85 (br, 1H, amide),5.80 (s, 1H, CH*H*=),5.66(s, 1H, C*H*H=),4.31 (s, 2H, allyl),4.20-4.11 (m, 1H, *N*-CH),1.21 (d, *J* = 6.5 Hz, 6H, CH$_3$).

14a: 28 wt% NH$_3$ aq (2.43 gm 40.0 mmol) was added dropwise to a solution of **13a** (1.27 g, 7.83 mmol) in 1,4-dioxane (7.0 mL) at 0 °C. The reaction mixture was poured into water (30 mL) and extracted with Et$_2$O (30 mL × 3). The combined organic layer was dried over MgSO$_4$, concentrated and dried in *vacuo* to give **14a** (0.625 g, 56.1% yield) as white powder.
^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ/ppm 7.48 (br, 0.25H, N*H*),7.08 (br, 0.75 H, N*H*), 5.93 (d, *J* = 0.94 Hz, 0.75 H, CH*H*=),5.92 (br, 0.25 Hz, CH*H*=), 5.43 (d, *J* = 0.75 H, 0.75 H, C*H*H=),5.40 (d, *J* = 0.75 H, 0.25 H, C*H*H=), 3.47 (s, 0.50 H, allyl),3.25 (s, 1.50 H, allyl), 3.20 (q, *J* = 7.5 Hz, 2H, *N*-C*H$_2$*),1.56 (m, *J* = 7.5 Hz, 2H, C*H$_2$*),0.92 (t, *J* = 7.5 Hz, 3H, C*H$_3$*).

14b was prepared from **12** (0.486 g, 3.01 mmol) in a similar manner to **14a** (0.163 g, 38.1%) as a white powder.
^{1}H NMR (400 MHz, 25 °C, CDCl$_3$) : δ 6.59 (d, 1H, *J* = 7.7 Hz, N*H*), 5.85 (s, 1H, CH*H*=), 5.50 (d, *J* = 1.0 Hz, 1 H, C*H*H=), 4.14-4.05 (m, *N*-CH), 3.42 (br, 1H, NH), 3.82 (s, 2H, allyl), 1.62 (br, 1H,NH), 1.19 (d, J = 6.7 Hz, 6H, CH$_3$).

Polymerization

A typical example (Table 2, Entry 3): A solution of **4b** (334 mg, 2.35 mmol), **5b** (84 mg, 0.74 mmol), AIBN (34 mg, 0.21 mmol) and small amount of octamethylcyclotetrasiloxane as an internal standard for ^{1}H NMR spectrum was dissolved in DMF (2.3 mL). After freeze-pump-thaw (FPT) cycling three times, the solution was heated 60 °C for 24 h. The mixture was poured into Et$_2$O (40 mL). The precipitate was collected and dried *in vacuo* to give the copolymer (236 mg, 56.5%). The monomer conversions were determined from the comparison of vinylidene and vinyl signals of **4b** and **5b** before and after the reaction against to the internal standard.

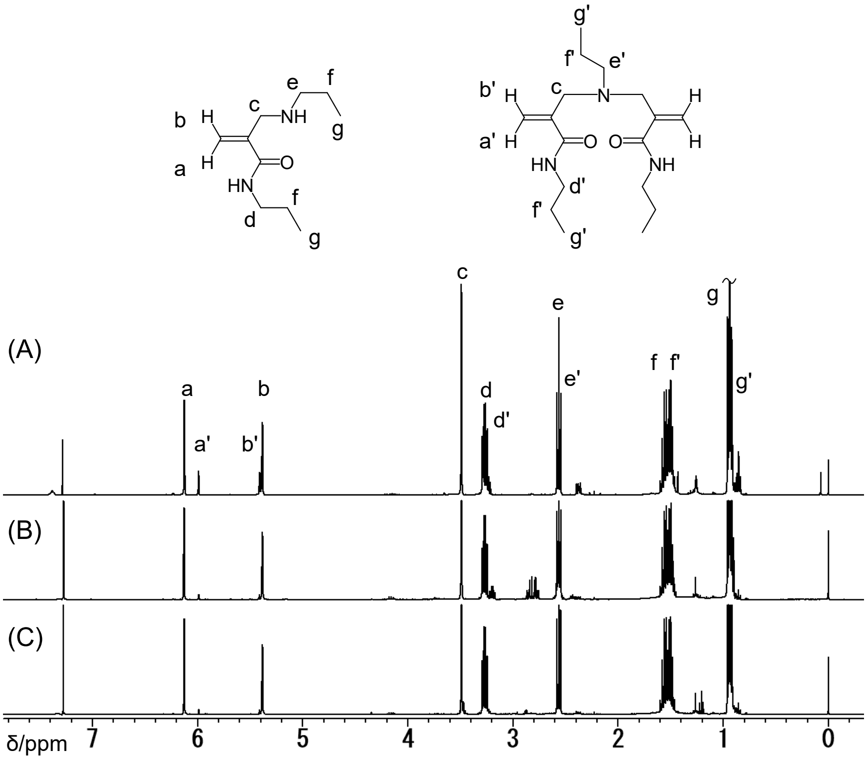


Fig. S1. ^{1}H NMR spectra of the extracted reaction mixture of **12** and *n*-propylamine (10 mole equivalent) at 25 °C (**A**), −20 °C (**B**) and −40 °C (**C**) (400 MHz, $CDCl_3$, 298 K).

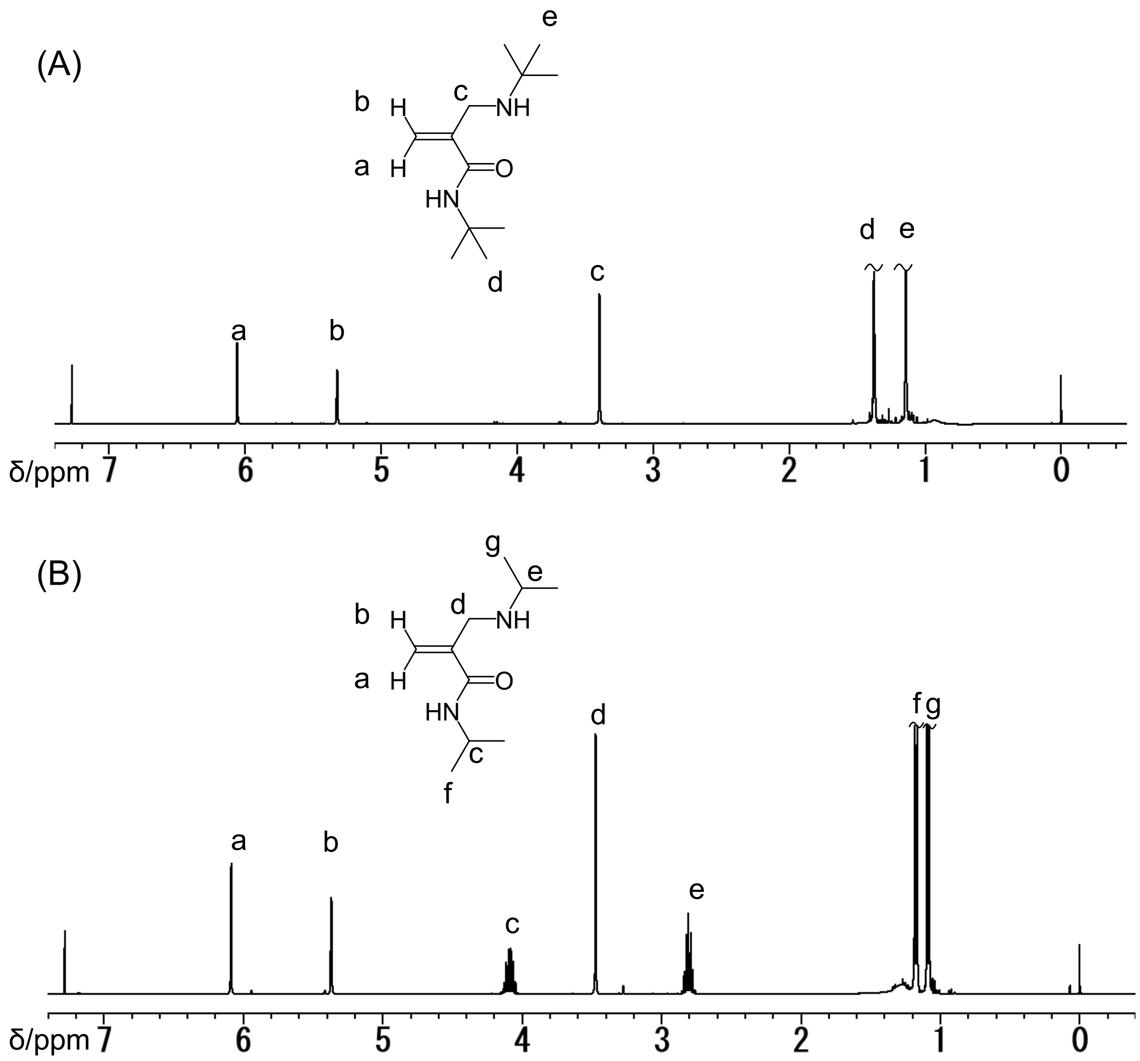


Fig. S2. ^{1}H NMR spectra of the extracted reaction mixture of **12** and *tert*-butylamine (**A**) and isopropylamine (**B**) at −20 °C (400 MHz, $CDCl_3$, 298 K).

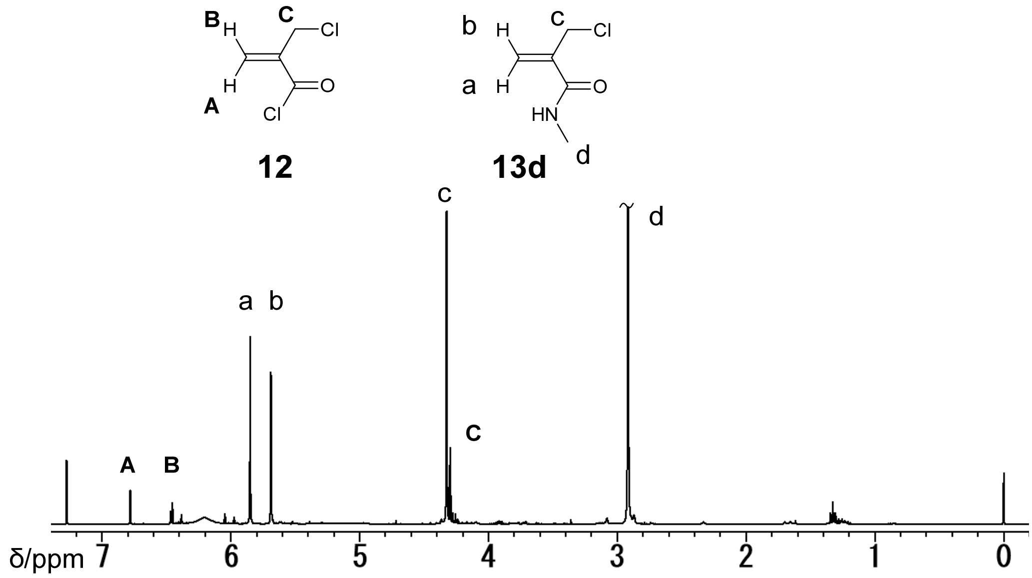


Fig. S3. ^{1}H NMR spectra of the extracted reaction mixture of **12** and methylamine at −40 °C (400 MHz, $CDCl_3$, 298 K).

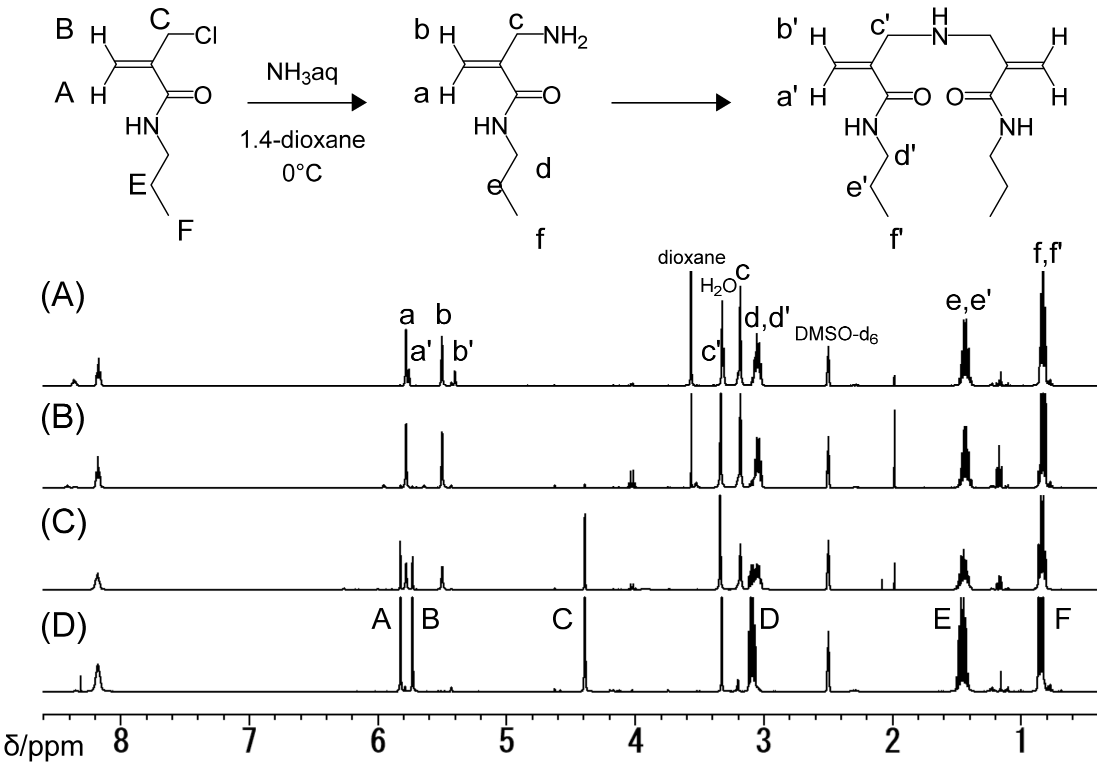


Fig. S4. ^{1}H NMR spectra of the extracted reaction products of **13a** and aqueous ammonia. The reaction conditions were at 25 °C for 16 h (**A**) and at 0 °C for 22 h (**B**) and 5 h (**C**). The ^{1}H NMR spectrum of **13a** (**D**) (400 MHz, $CDCl_3$, 298 K).

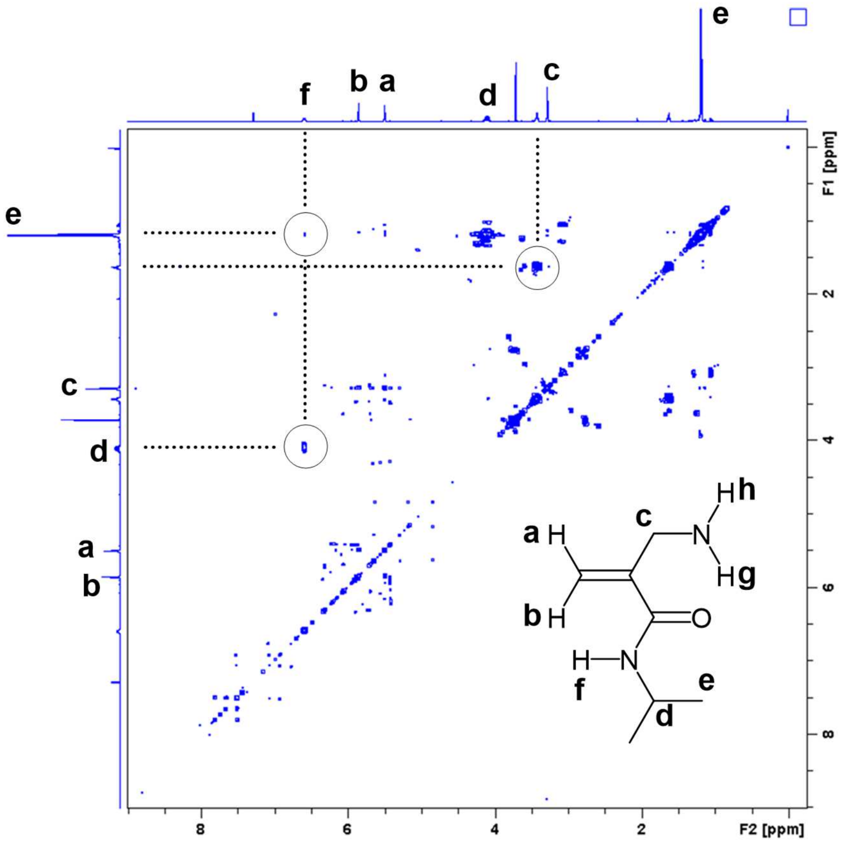


Fig. S5. ^{1}H COSY NMR spectrum of **4b** (400 MHz, $CDCl_3$, 298 K).

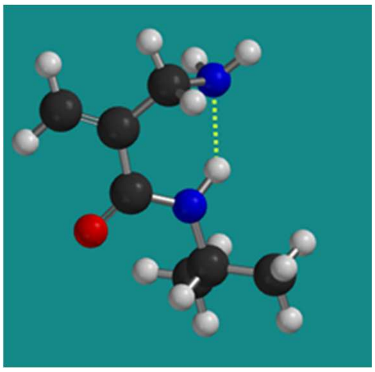


Fig. S6. The most stable conformation of **4b** simulated by conformer search function using molecular mechanics under MMFF force field and the geometry optimization by DFT calculation (B3LYP/6-31G*). All simulations were performed by Spartan 20 (Wavefunction Inc.).

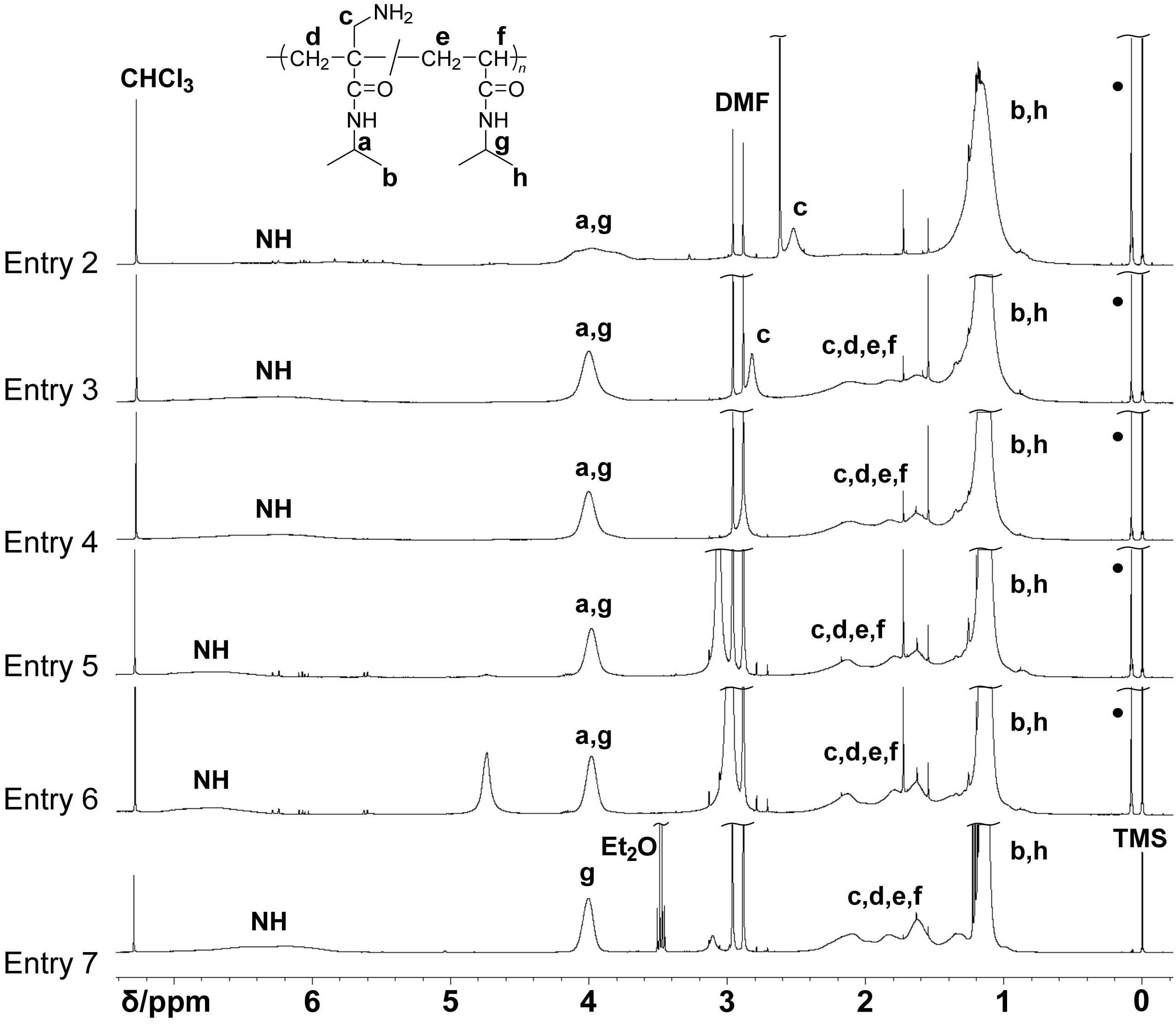


Fig. S7. ^{1}H NMR spectra of **poly(4b-*co*-5b)** (400 MHz, $CDCl_3$, 298 K). ●: Octamethylcyclotetrasiloxane used as a standard to determine monomer conversions.

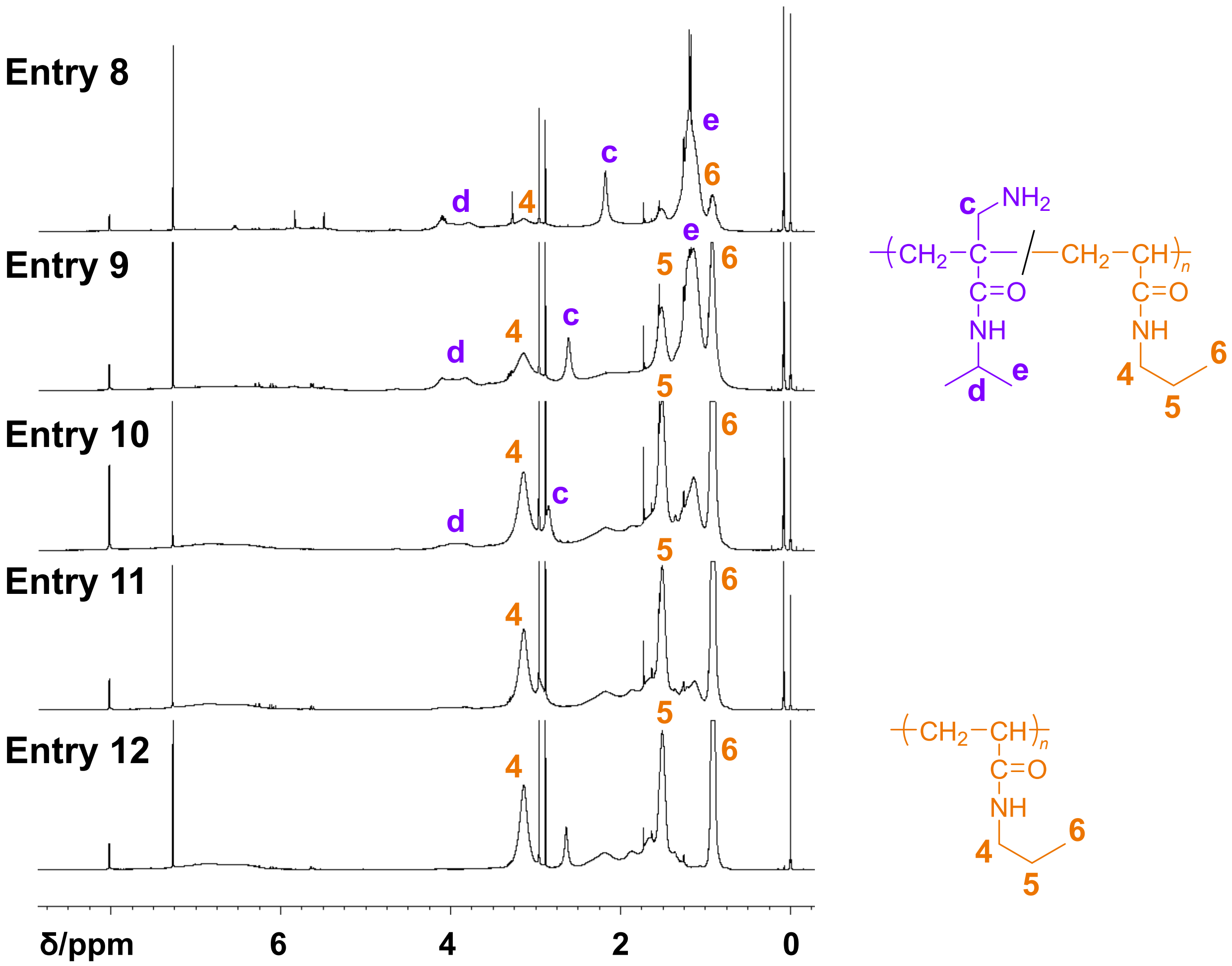


Fig. S8. ^{1}H NMR spectra of **poly(4b-*co*-5a)** (400 MHz, $CDCl_3$, 298 K).

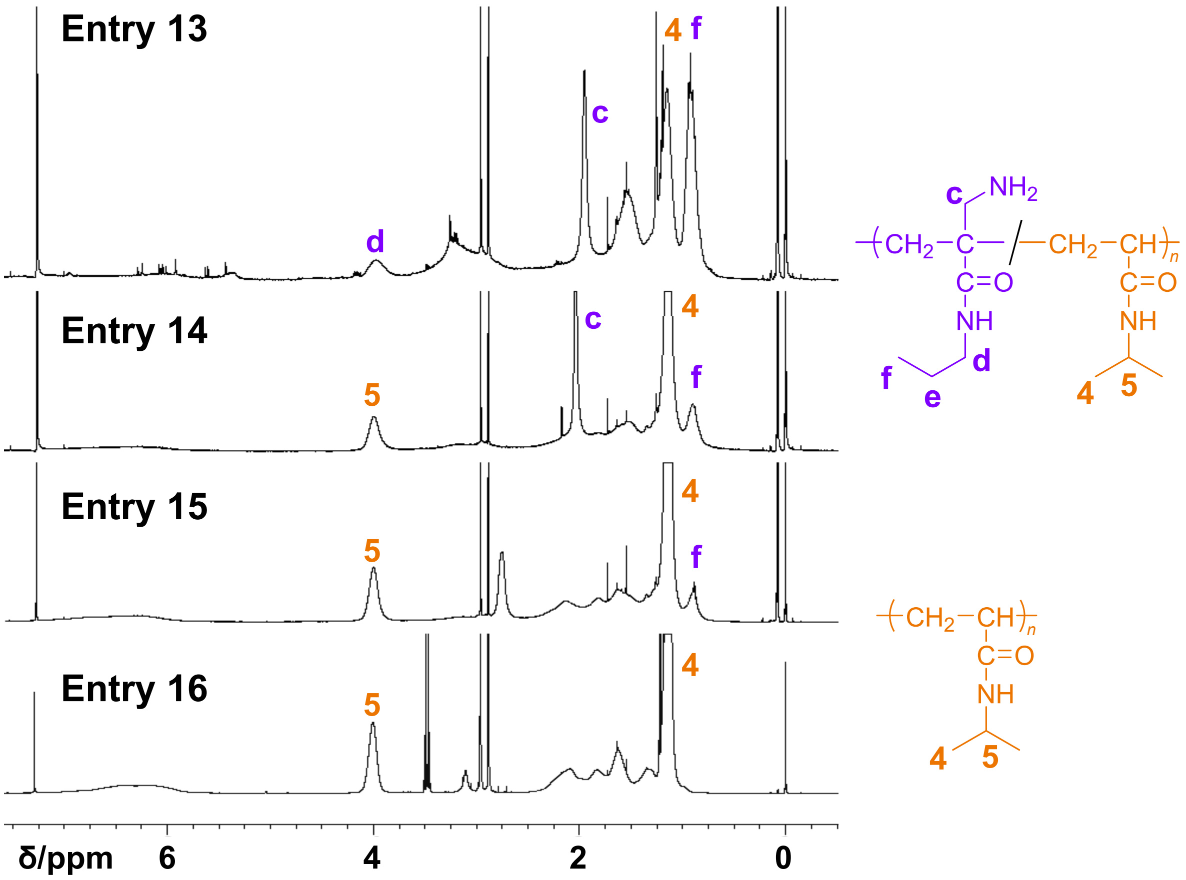


Fig. S9. ^{1}H NMR spectra of **poly(4a-*co*-5b)** (400 MHz, $CDCl_3$, 298 K).

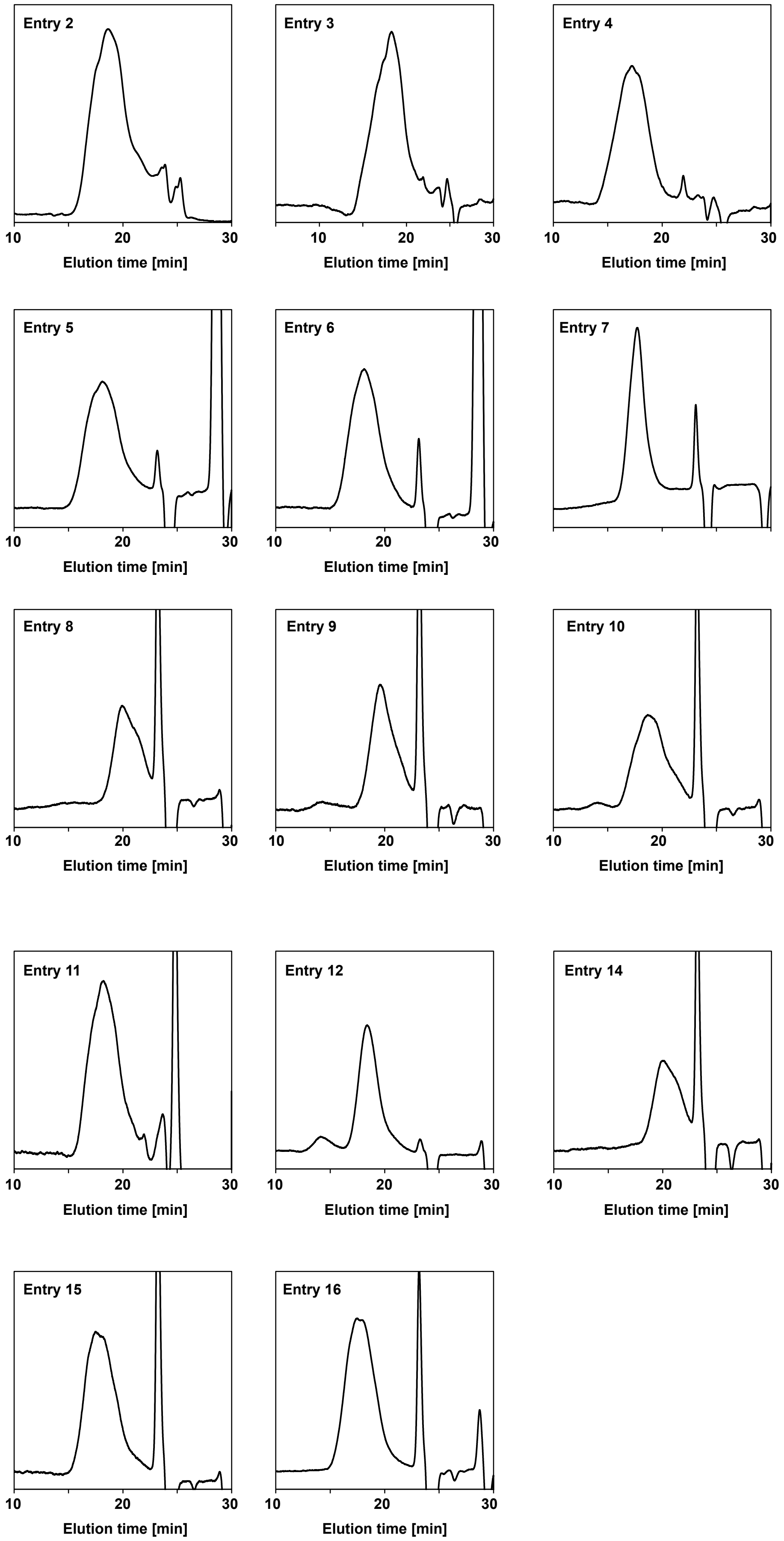
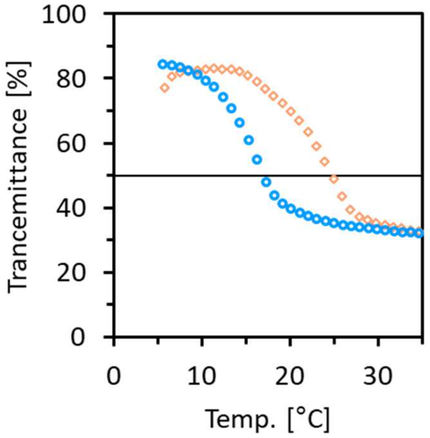
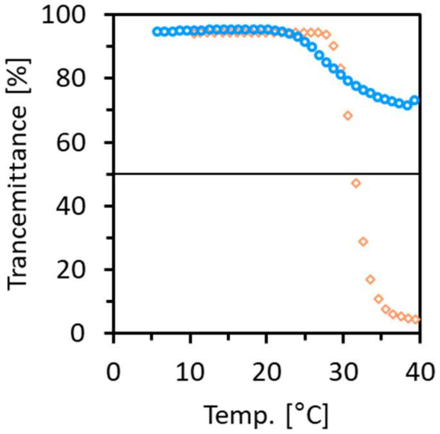
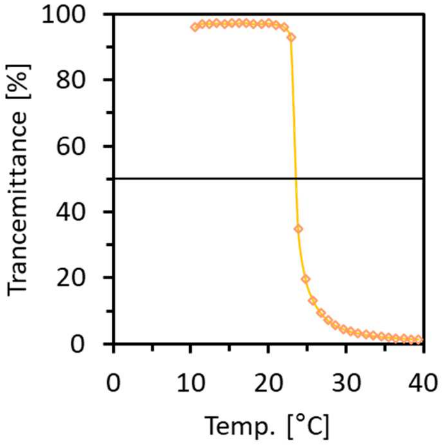
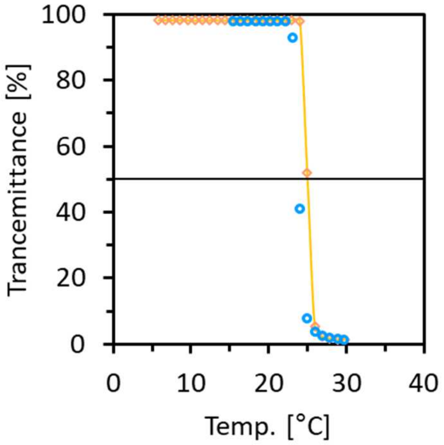
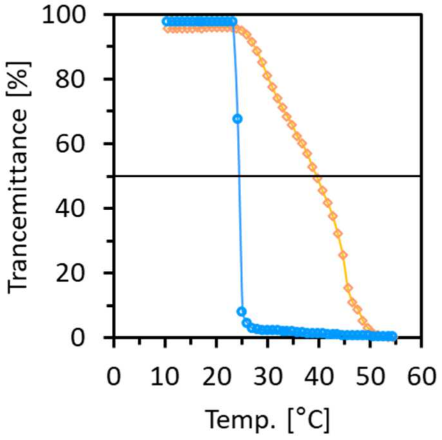
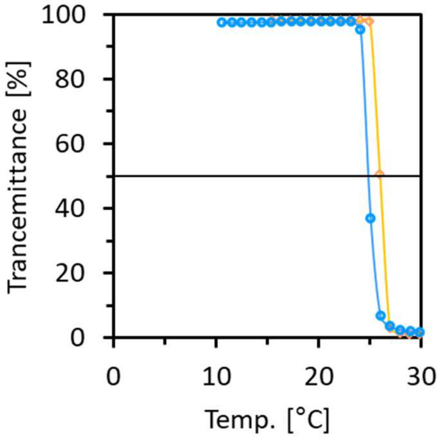
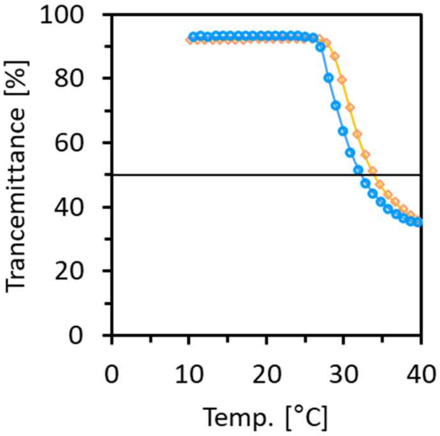
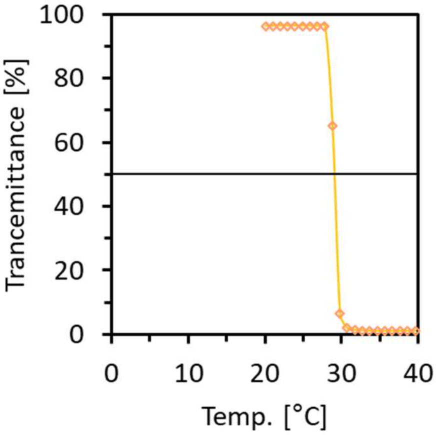
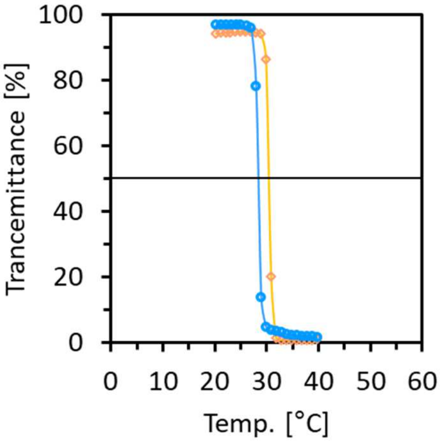
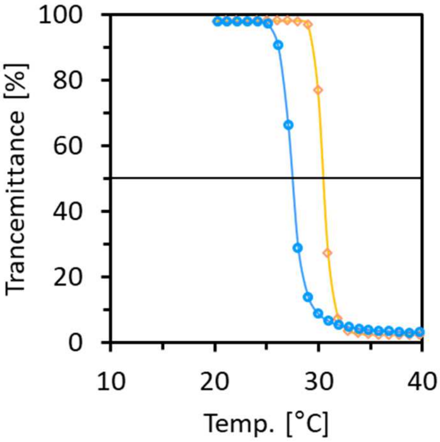
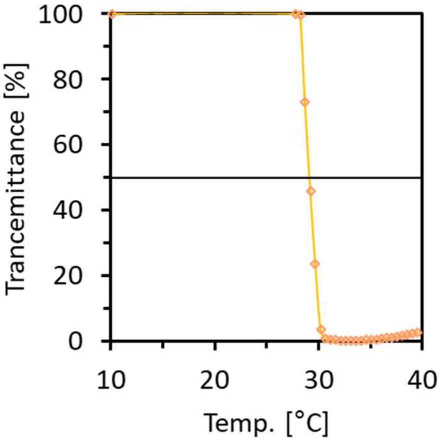
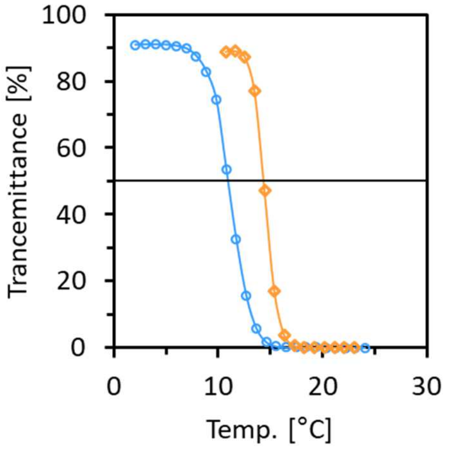
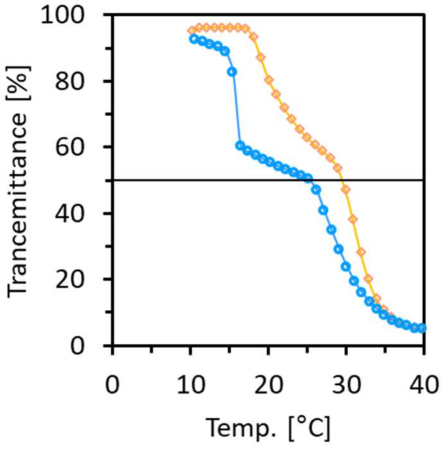
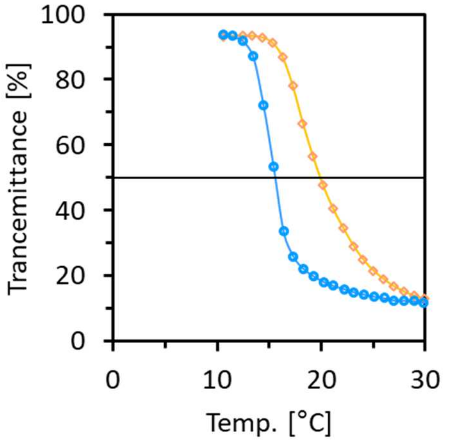
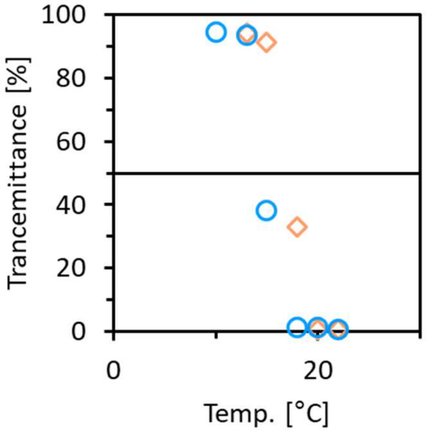
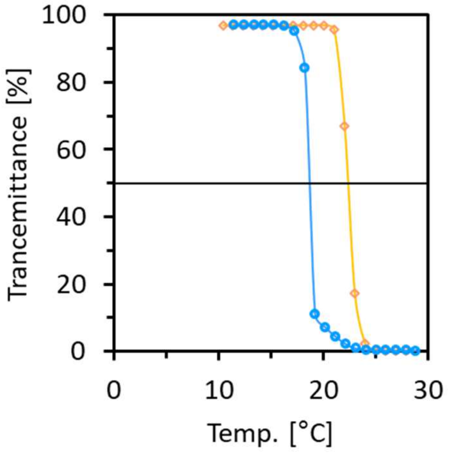
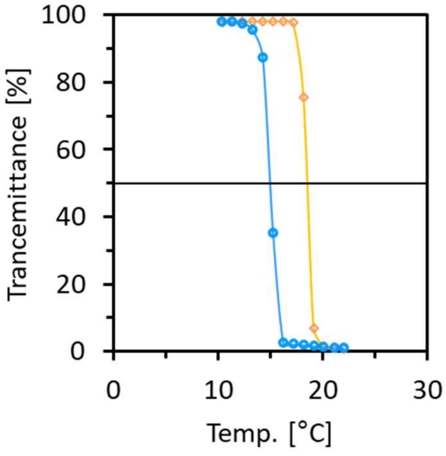


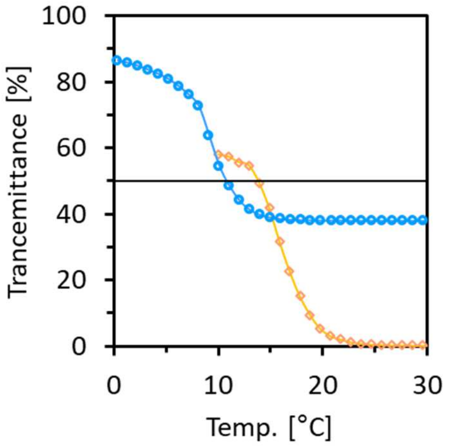
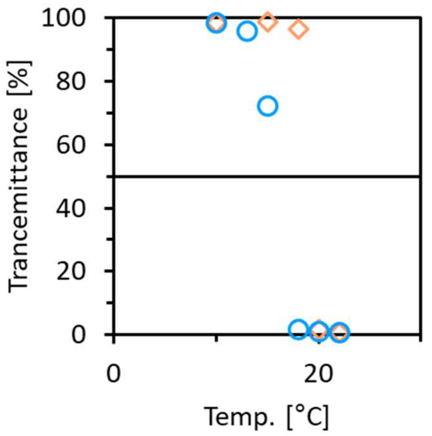
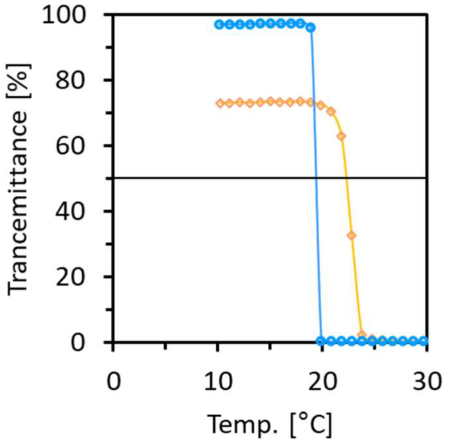
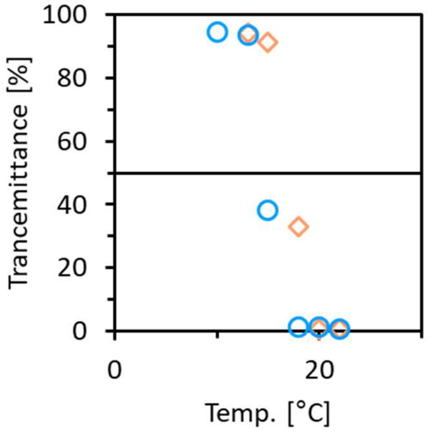
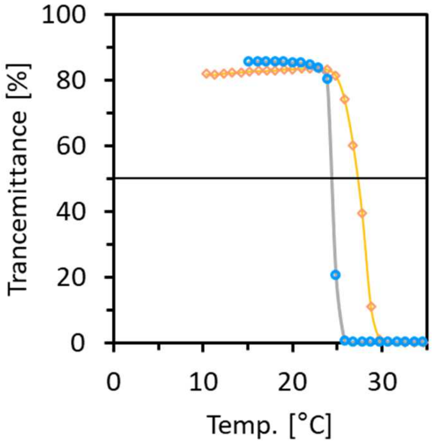
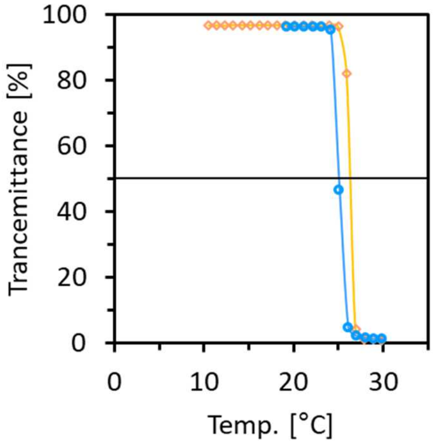
Fig. S10. SEC curves of the obtained polymers. The entries are corresponding to those in Table 2.

Table S1. Changes of transmittance of **poly(4-*co*-5)** in H_2O and 1 M HCl aq.

Entry	In H_2O	In 1M HCl aq
2		
3		
4		

5	Trancemittance [%] 0 20 40 60 80 100 Temp. [°C] 0 10 20 30 40	Trancemittance [%] 0 20 40 60 80 100 Temp. [°C] 0 10 20 30 40
6	Trancemittance [%] 0 20 40 60 80 100 Temp. [°C] 0 10 20 30 40 50 60	Trancemittance [%] 0 20 40 60 80 100 Temp. [°C] 10 20 30 40
7		Trancemittance [%] 0 20 40 60 80 100 Temp. [°C] 10 20 30 40

9	Trancemittance [%] 100 80 60 40 20 0 0 10 20 30 Temp. [°C]	Trancemittance [%] 100 80 60 40 20 0 0 10 20 30 40 Temp. [°C]
10	Trancemittance [%] 100 80 60 40 20 0 0 10 20 30 Temp. [°C]	Trancemittance [%] 100 80 60 40 20 0 0 20 Temp. [°C]
12	Trancemittance [%] 100 80 60 40 20 0 0 10 20 30 Temp. [°C]	Trancemittance [%] 100 80 60 40 20 0 0 10 20 30 Temp. [°C]

14		
15		
16		

References

1 Y. Kohsaka, T. Miyazaki, K. Hagiwara, *Polym. Chem.*, 2018, **9**, 1610