Supplementary Information for

Property Modulation of Poly(vinyl alcohol)s via Controlled Incorporation of α-Methyl Groups Using Alkenylboron Monomers

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1 General Information

Materials

For monomer synthesis: Isatoic anhydride (TCI, >98%), 2-methoxyethylamine (TCI, >98%), potassium vinyltrifluoroborate (TCI, >97%), ethylamine trifluoroborane (TCI, >97%), ultrapure water (Wako), tetrahydrofuran (THF: Wako, with stabilizer, >99.5%), dichloromethane (DCM: Wako, >99.5%), toluene (Wako, deoxidized, >99.5%), cyclopentyl methyl ether (CPME: Wako, super dehydrated, with stabilizer, >99%), sodium chloride (NaCl: Wako, >99.5%), sodium sulfate (Na_2SO_4: Wako, anhydrous, >99%) were used as received. For purifications using column chromatography, Wako gel C-200 (Wako), *n*-hexane (Wako, >96%), and ethyl acetate (EtOAc: Wako, >99.5%) were used.

For radical polymerization: 2-Isopropenylboronic acid pinacol ester (IPBpin: TCI, >98%), vinylboronic acid pinacol ester (VBpin: TCI, stabilized with phenothiazine, >93%), vinyl acetate (VAc: TCI, stabilized with hydroquinone, >99%), and isopropenyl acetate (IPAc: TCI, >98%) were purified by distillation prior to use as monomers for radical polymerization. Dibenzyl ether (Bn_2O: TCI, >95%; internal standard for ^1H NMR) was purified by distillation prior to use. 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70: Wako, >95%) was used as received for radical initiators. For a chain transfer agent in RAFT polymerization, 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT: Aldrich, >97%) was used as received. *N,N*-dimethylformamide (DMF: Wako, deoxidized, >99.5%) was used for polymerization solvent without further purification. For purification of the obtained polymers by reprecipitation, diethyl ether (Et_2O: Wako, >99.5%) and acetonitrile (CH_3CN: Wako, >99.5%) were used as received.

For protecting group replacement: Pinacol (TCI, >98%), *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$: TCI, >98%), and THF (Wako, with stabilizer, >99.5%) were used as received. For dialysis after the protecting group replacement, MWCO3500 (Spectra/PorVR7, diameter 29 mm) and acetone (Wako, >99%) were used.

For post-polymerization oxidation: Sodium hydroxide (NaOH: Wako, >97%), hydrogen peroxide (H_2O_2: TCI, 35% in H_2O), ultrapure water (Wako), ethanol (EtOH: Wako, >99,5%), THF (Wako, with stabilizer, >99.5%), and acetic acid (Wako, >99.7%) were used as received. For dialysis after the oxidation reaction, MWCO1000 (Spectra/PorVR7, diameter 29 mm) and methanol (Wako, >99.5%) were used.

Measurements

^1H, ^{13}C, and ^{11}B NMR: NMR spectra were recorded on a JEOL JNM-ECZ400S spectrometer operating at 398.98 MHz (^1H), 100.32 MHz (^{13}C), and 128.01 MHz (^{11}B) at room temperature. Chloroform-*d* [$CDCl_3$: Wako, D, 99.8%, +0.05 vol% tetramethyl silane] and dimethyl sulfoxide-d_6 (DMSO-d_6: Wako, D, 99.9%) were used as deuterated solvents. For an internal standard in ^{11}B NMR, boron trifluoride-ethyl ether complex ($BF_3{\cdot}Et_2O$) sealed in a capillary was used. The chemical shifts of the NMR spectra are reported in parts per million (ppm) using tetramethyl silane (TMS) or residual solvent signals as references [$CDCl_3$: δ H = 0.00 ppm (TMS), δ C = 77.16 ppm, δ B = 0.00 ppm ($BF_3{\cdot}Et_2O$)/DMSO-d_6: δ H = 2.50 ppm, δ C = 39.52 ppm]. All coupling constants (*J* values) are reported in Hertz (Hz). Data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sep = septet, m = multiplet, brs = broad singlet).

Infrared spectroscopy (IR): IR spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer equipped with ATR attachment.

Electrospray ionization-mass spectrometry (ESI-MS): ESI-MS analysis was performed on an Exactive Plus (LC-MS spectrometer, Thermo Fisher Scientific).

Size-exclusion chromatography (SEC): For the polymers in which the boron units are protected by anthranilamide derivatives, SEC curves, number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution ($Đ$) were measured by SEC in DMF containing 10 mM LiBr at 40 ℃ (flow rate: 1 mL/min) on two polystyrene gel columns (Shodex K-805L) that were connected to a JASCO PU-4580 precision pump, a JASCO RI-4030 refractive index detector, and a JASCO UV-4575 UV/vis detector set at 254 nm. The columns were calibrated against eleven standard poly(MMA) samples (PSS Ready Cal Kit: M_p = 2380–2200000). For the polymers without anthranilamide-protected boron pendants, SEC curves, M_n, M_w, and $Đ$ were measured by SEC in THF at 40 °C (flow rate: 0.35 mL/min) on two polystyrene gel columns (Shodex LF-404) that were connected to an HLC-8320GPC system (TOSOH). The columns were calibrated against eleven standard poly(MMA) samples (PSS Ready Cal Kit: M_p = 800–2200000).

Differential scanning calorimetry (DSC): These measurements were performed on a DSC Q200 calorimeter (TA instrument) equipped with an RCS 90 electric machine under a flow of dry nitrogen. The polymer sample (ca. 1–3 mg) was placed into an aluminum pan. The temperature program was as follows:

> For VA–IPA (co)polymer (VA content: 84, 73, 57, 45, 31, 18mol%): first heating from 40 °C to 230 °C (10 °C/min) → equilibration at 230 °C for 5 min → first cooling from 230 °C to 0 °C (5 °C/min) → equilibration at 0 °C for 5 min → second heating from 0 °C to 250 °C (10 °C/min).
>
> For VA–IPA (co)polymer (VA content: 100, 7, 0 mol%): first heating from 40 °C to 180 °C (10 °C/min) → equilibration at 180 °C for 15 min → first cooling from 230 °C to 0 °C (5 °C/min) → equilibration at 0 °C for 5 min → second heating from 0 °C to 250 °C (10 °C/min).

The second heating scan was employed to determine the T_g and T_m of polymer samples.

X-Ray Diffraction (XRD): XRD spectra were recorded on an Aeris (Malvern) operating at 40 kV and 15 mA. Cu Kα radiation (λ = 0.154 nm). The scattering angle 2θ scanning rate was set to 0.0435°/s in a range of 5–60°. Polymer samples were annealed at 100 °C for 1.5 h and cooled to room temperature before measurements.

Ultraviolet-visible absorption spectroscopy (UV-vis): Transmittance of polymer solutions were recorded on JASCO V-750 spectrophotometer (optical length: 1.0 cm). The polymer samples for transmittance measurement were dissolved in solvent [water (Wako, ultrapure water) or acetone (Nacalai Tesque, >99.5%)], heated or cooled until the polymer visually dissolved.

Dynamic Light Scattering (DLS): DLS was measured on Malvern Zetasizer Nano equipped with a HeNe laser (wavelength: 633 nm). The measuring angle was 173° and the data was analyzed by cumulant method. The polymer solution samples were prepared by the same method as for the transmittance measurement. The measurement was done three times every 5 °C on heating (for water) or cooling (for acetone) process, and the averaged D_h values were calculated.

2 Experimental Procedures

Monomer Synthesis

Anthranilamide derivative with with 2-methoxyethyl group as a substituent on the amide group (aam-MOE) and corresponding anthranilamide-protected vinylboronic acid (VBaam-MOE) were synthesized according to the literature (Reference 25 in the main text). In brief, aam-MOE was prepared through addition-decarboxylation of 2-methoxyethylamide to isatoic anhydride at room temperature in THF/H_2O. The product was purified by extraction (DCM/NaCl aq.) and used for the next reaction. The obtained aam-MOE was treated with potassium vinyltrifluoroborate in the presence of ethylamine trifluoroborane at 100 °C in toluene/CPME under Ar atmosphere. The product was purified by extraction (EtOAc/NaCl aq.) and column chromatography on silica gel (eluent: *n*-hexane/EtOAc).

Free Radical (Co)polymerization of Vinyl Monomer with Isopropenyl Monomer

The polymerization was performed in DMF using V-70 as an initiator under an inert gas atmosphere. The typical procedure for the copolymerization of VBaam-MOE with IPBpin ($[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0$ = 1/1) at 30 °C was as follows: VBaam-MOE (345 mg, 1.50 mmol) was placed in a Schlenk tube with a PTFE stopcock (J. Young). Then IPBpin (282 μL, 252 mg, 1.50 mmol), dibenzyl ether (28.3 μL, 29.7 mg, 150 μmol), DMF (882 μL), and a DMF solution of V-70 (463 μL of 20 mg/mL, 9.25 mg, 30.0 μmol) were added at room temperature under a dry argon atmosphere. The reaction mixture was stirred at 30 °C in a water bath. After 48 h, the polymerization was terminated by cooling in dry ice-methanol. The conversions of both monomers were monitored by ^{1}H NMR spectroscopy: Conv. (VBaam-MOE) = 85% , Conv. (IPBpin) = 89% after 48 h. The M_n, M_w, and $Đ$ of the resultant polymer was determined by the SEC analysis: $M_n = 16.0 \times 10^3$, $M_w = 31.3 \times 10^3$, $Đ = 1.96$. Copolymerization of other monomers (VBpin, IPBpin, VAc, and IPAc) were also performed similarly. The copolymerization of VAc with IPAc was also conducted without solvent (bulk polymerization).

The (co)polymerization of VBaam-MOE with IPBpin with various monomer feed ratios was performed under the following conditions. The quenched reaction mixture was diluted by DCM and poured into diethyl ether or acetonitrile to purify by reprecipitation.

VBaam-MOE/IPBpin = 100/0: $[\text{VBaam-MOE}]_0/[\text{V-70}]_0$ = 1500/15 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 90/10: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1364/136/15 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 80/20: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1200/300/15 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 67/33: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1000/500/15 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 50/50: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 750/750/15 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 33/67: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 667/1333/20 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 20/80: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 500/2000/25 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 9/91: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 273/2727/30 mM in DMF at 30 °C for 48 h.
VBaam-MOE/IPBpin = 0/100: $[\text{IPBpin}]_0/[\text{V-70}]_0$ = 3000/30 mM in DMF at 30 °C for 48 h.

RAFT Copolymerization of VBaam-MOE with IPBpin

The typical procedure for the RAFT copolymerization of VBaam-MOE with IPBpin ([VBaam-MOE]$_0$/[IPBpin]$_0$ = 1/1) using CPDT as a chain transfer agent (CTA) was as follows: VBaam-MOE (173 mg, 0.75 mmol) was placed in a Schlenk tube with a PTFE stopcock (J. Young). Then IPBpin (141 μL, 126 mg, 0.75 mmol), dibenzyl ether (14.2 μL, 14.9 mg, 75 μmol), DMF (244 μL), CPDT (5.2 μL, 5.2 mg, 15 μmol), and a DMF solution of V-70 (23.1 μL of 40 mg/mL, 0.93 mg, 3 μmol) were added at room temperature under a dry argon atmosphere. The reaction mixture was stirred at 30 °C in a water bath. After 48 h, the polymerization was terminated by cooling in dry ice-methanol. The conversions of both monomers were monitored by ^{1}H NMR spectroscopy: Conv. (VBaam-MOE) = 87% , Conv. (IPBpin) = 93% after 48 h. The M_n, M_w, and $Đ$ of the resultant polymer was determined by the SEC analysis: $M_n = 8.9 \times 10^3$, $M_w = 12.5 \times 10^3$, $Đ = 1.40$. in 48 h. Copolymerization in different monomer feed ratios ([VBaam-MOE]$_0$/[IPBpin]$_0$ = 2/1 and 1/2) were also performed similarly.

Replacement of Protecting Groups (aam-MOE → pin) within the VBaam-MOE–IPBpin (Co)polymers

The typical procedure for the protecting group replacement of VBaam-MOE–IPBpin copolymer (VBaam-MOE : IPBpin = 48 : 52) was as follows: VBaam-MOE–IPBpin copolymer was synthesized by the typical free radical polymerization method and purified by reprecipitation into diethyl ether (polymerization condition: [VBaam-MOE]$_0$/[IPBpin]$_0$/[V-70]$_0$ = 750/750/15 mM in DMF at 30 °C for 48 h). The resulting copolymer (400 mg, $M_n = 17.3 \times 10^3$, $Đ = 1.75$), pinacol (1.15 g, 9.74 mmol, 10 eq. for the VBaam-MOE units), and *p*-toluenesulfonic acid monohydrate (556 mg, 2.92 mmol, 3 eq. for the VBaam-MOE units) were dissolved in THF (9.74 mL, 10 mL/mmol for the VBaam-MOE units). The reaction mixture was stirred at 60 °C in an oil bath under ambient atmosphere. After 24 h, the products were subjected several times to dialysis (solvent: acetone) to remove any residues of low molecular weight compounds. The solvent was removed by evaporation and the polymer was obtained as a brown solid (295 mg). Although the replacement reaction did not procced quantitatively (The unit ratio was determined as VBpin : VBaam-MOE : IPBpin = 36 : 12 : 52, based on ^{1}H NMR spectra), the resulting copolymer was subjected to the subsequent side-chain oxidation. The protecting group replacement of VBaam-MOE–IPBpin (co)polymers with other composition ratios was performed in a similar way.

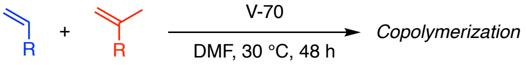
Oxidation of VBpin–VBaam-MOE–IPBpin (Co)polymers

The typical procedure for the oxidation of VBpin–VBaam-MOE–IPBpin copolymer (VBpin : VBaam-MOE : IPBpin = 36 : 12 : 52) was as follows: The copolymer after the replacement of anthranilamide-protection to pinacol (280 mg) was dissolved in THF (20 mL). Then, ethanol (4.0 mL), an aqueous solution of NaOH (6 M, 0.68 mL), and an aqueous solution of H_2O_2 (35wt%, 0.85 mL) were added. The reaction solution was stirred at room temperature under atmospheric condition. After 8 h, the precipitated polymer was collected and subjected to dialysis in order to remove any residues of low molecular weight compounds: Dialysis was performed several times with substitution of the solvent in the following order: water/MeOH = 50/50 (v/v) → water/MeOH = 30/70 (v/v) → MeOH → MeOH. The solvent was removed by evaporation and VA–IPA copolymer was obtained as a colorless solid (61.2 mg). The oxidation of other (co)polymers was performed in a similar way. Reagent concentrations and reaction times are as follows:

(VBaam-MOE+VBpin)/IPBpin = 100/0: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 5 h.
(VBaam-MOE+VBpin)/IPBpin = 90/10: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 8 h.
(VBaam-MOE+VBpin)/IPBpin = 78/22: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 8 h.
(VBaam-MOE+VBpin)/IPBpin = 64/36: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 8 h.
(VBaam-MOE+VBpin)/IPBpin = 48/52: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 8 h.
(VBaam-MOE+VBpin)/IPBpin = 33/67: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/390/156 mM, 8 h.

(VBaam-MOE+VBpin)/IPBpin = 21/78: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/780/156 mM, 24 h.
(VBaam-MOE+VBpin)/IPBpin = 9/91: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/3900/780 mM, 24 h.
(VBaam-MOE+VBpin)/IPBpin = 0/100: [repeating units]$_0$/[H_2O_2]$_0$/[NaOH]$_0$ = 78/3900/780 mM, 24 h.

3 Radical Copolymerization of Vinyl and Isopropenyl Monomers



$[\text{vinyl monomer}]_0/[\text{isopropenyl monomer}]_0/[\text{V-70}]_0$ = 750/750/15 mM in DMF at 30 °C.

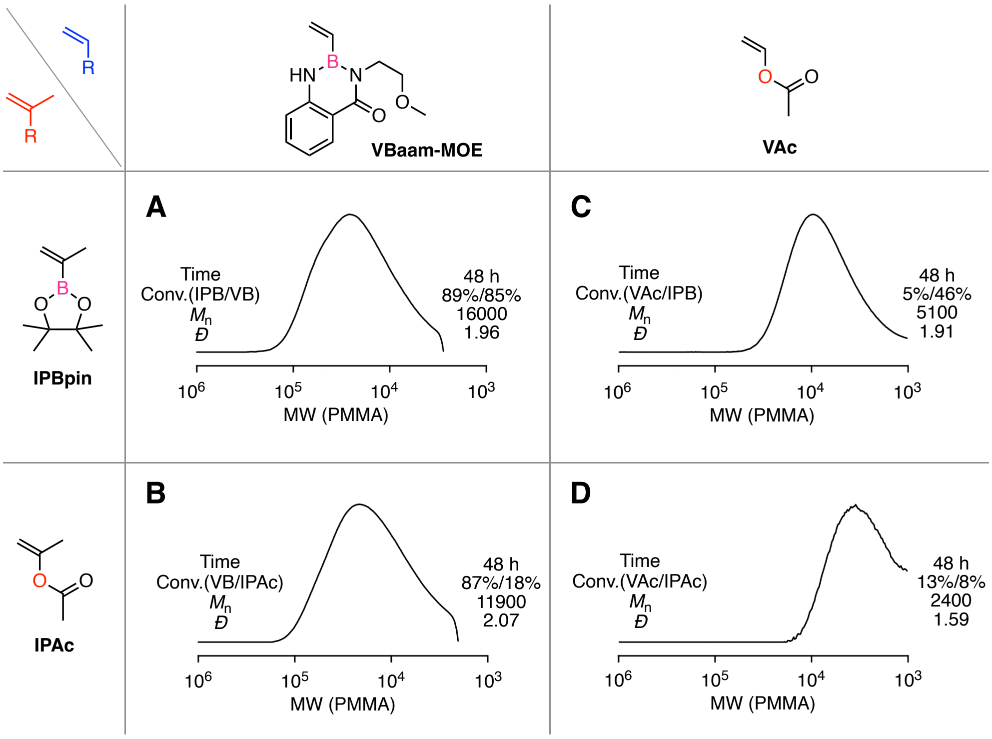


Figure S1. SEC traces for free radical copolymerization of (A) VBaam-MOE–IPBpin, (B) VBaam-MOE–IPAc, (C) VAc–IPBpin, and (D) VAc–IPAc (described in Figure 2A). Polymerization condition: $[\text{vinyl monomer}]_0/[\text{isopropenyl monomer}]_0/[\text{V-70}]_0$ = 750/750/15 mM in DMF at 30 °C.

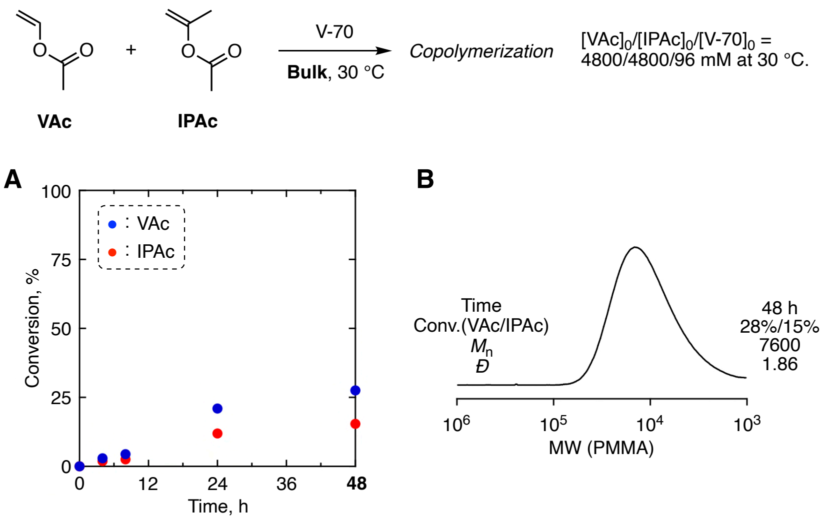


Figure S2. Free radical copolymerization of VAc and IPAc (bulk condition). (A) Time-conversion plot. (B) SEC trace for the polymerization. Polymerization condition: $[VAc]_0/[IPAc]_0/[V\text{-}70]_0$ = 4800/4800/96 mM at 30 °C.

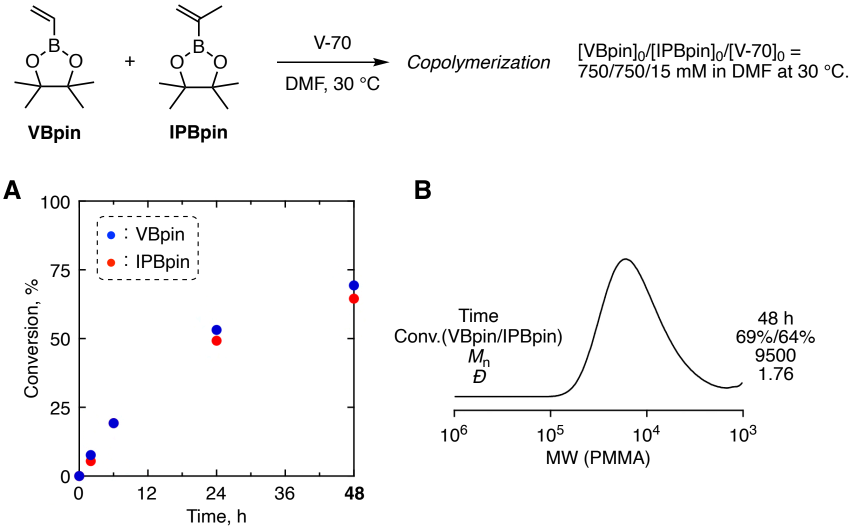


Figure S3. Free radical copolymerization of VBpin and IPBpin. (A) Time-conversion plot. (B) SEC trace for the polymerization. Polymerization condition: $[VBpin]_0/[IPBpin]_0/[V\text{-}70]_0$ = 750/750/15 mM in DMF at 30 °C.

Table S1. Free radical copolymerization of IPBpin with VBaam-MOE or VBpin with varying monomer feed ratios[a]

Entry	Vinyl monomer	VB/IPB (feed)[b]	Conv.$_{\mathrm{VB}}$, %[c]	Conv.$_{\mathrm{IPB}}$, %[c]	M_n[d]	$Đ$[d]
1	VBaam-MOE[e]	81.2/18.8	91	100	23300	2.10
2		67.4/32.6	88	95	18400	2.03
3		33.1/66.9	82	79	14600	1.85
4		19.8/80.2	82	70	12600	1.77
5	VBpin[f]	79.1/20.9	47	41	4400	1.71
6		69.8/30.2	64	58	6900	1.72
7		32.7/67.3	72	66	11400	1.81
8		22.0/78.0	74	64	11900	1.83

[a] Polymerization condition: $[(\text{VBaam-MOE or VBpin}) + \text{IPBpin}]_0/[\text{V-70}]_0 = 1500/15$ mM in DMF at 30 °C for 48 h. [b] Actual monomer feed ratios determined by ^{1}H NMR measurement. [c] Monomer conversion at the time of termination of polymerization determined by ^{1}H NMR measurement. [d] Number-average molecular weight (M_n) and molecular weight distribution ($Đ$) of the resulting polymers determined by SEC with PMMA standard calibration. [e] SEC measurement was performed using DMF with 10 mM LiBr as eluent for SEC measurement. [f] SEC measurement was performed using THF as eluent.

4 Determination of Monomer Reactivity Ratios

Monomer reactivity ratios were determined based on the report by Mayo and Lewis.[1] The copolymerization behavior of two monomers (M_1 and M_2) is generally described based on equation (1), where $[M_1]$ is the concentration of M_1, $[M_2]$ is the concentration of M_2, and r_1 and r_2 are the reactivity ratios of M_1 and M_2.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} \qquad (1)$$

When the monomer consumption is sufficiently small, the Mayo–Lewis equation shown above can be approximated to

$$\frac{\Delta[M_1]}{\Delta[M_2]} \doteqdot \frac{[M_1]_0(r_1[M_1]_0 + [M_2]_0)}{[M_2]_0(r_2[M_2]_0 + [M_1]_0)} \qquad (2)$$

where $[M_1]_0$ is the concentration of M_1 before the reaction, $[M_2]_0$ is the concentration of M_2 before the reaction, $\Delta[M_1]$ is the consumption of M_1 during the reaction, and $\Delta[M_2]$ is the consumption of M_2 during the reaction.

When F_1 is defined as the composition of M_1 in the consumed monomers during the reaction ($F_1 = \Delta[M_1]/(\Delta[M_1]+\Delta[M_2])$, $F_2 = \Delta[M_2]/(\Delta[M_1]+\Delta[M_2])$), and f_1 as the composition of M_1 in the monomer feed before the reaction ($f_1 = [M_1]_0/([M_1]_0+[M_2]_0)$, $f_2 = [M_2]_0/([M_1]_0+[M_2]_0)$), equation (2) can be expressed as:[2,3]

$$F_1 = \frac{r_1 {f_1}^2 + f_1(1 - f_1)}{r_1 {f_1}^2 + 2f_1(1 - f_1) + r_2(1 - f_1)^2} \qquad (3)$$

On the basis of equation (3) and the experimental results obtained for f_1 and F_1, nonlinear least-squares fitting of f_1 versus F_1 was performed using the Solver Function in Microsoft Office Excel. The sums of the squares of the deviation were minimized by optimizing r_1 and r_2. The experimental procedure to obtain f_1 and F_1 series in each copolymerization is shown in following section.

The copolymerization of VBaam-MOE and IPBpin was performed using V-70. The sum of the concentrations of both monomers was 1500 mM, and the feed ratio of each monomer was varied ([VBaam-MOE]$_0$:[IPBpin]$_0$ = 90:10, 70:30, 50:50, 30:70, and 10:90). A typical procedure for the copolymerization for the determination of the monomer reactivity ratios was as follows: VBaam-MOE (69.0 mg, 0.3 mmol), IPBpin (56.4 µL, 50.4 mg, 0.3 mmol), dibenzyl ether (5.7 µL, 6.0 mg, 30 µmol, internal standard), and DMF (176 µL) were placed in a Schlenk tube with a PTFE stopcock (J. Young) under a dry argon atmosphere. A DMF solution of V-70 (20 mg/mL, 92.5 µL, 1.85 mg, 6 µmol) was then added at room temperature. (5:5 feed ratio condition). The reaction mixture was placed in an oil bath at 30 °C. After 45 min, the solution was cooled to −25 °C to terminate the polymerization. The composition ratio [$F = DP_{\text{VBaam-MOE}}/(DP_{\text{VBaam-MOE}} + DP_{\text{IPBpin}})$] was determined from the monomer conversion ratio [Conv.(VBaam-MOE)/(Conv.(VBaam-MOE) + Conv.(IPBpin))] by ^{1}H NMR spectroscopy ($CDCl_3$) with dibenzyl ether as the internal standard. The actual monomer feed ratio [f = [VBaam-MOE]$_0$/([VBaam-MOE]$_0$ + [IPBpin]$_0$) was also determined from ^{1}H NMR spectroscopy (before heating). The obtained series of f_1 and F_1 values were used to determine r_1 and r_2 on the basis of equation (3) through the non-linear least-squares method (*vide supra*), affording the monomer reactivity ratios. The monomer conversions are summarized in the following table.

Table S2. Free radical copolymerization of VBaam-MOE (M_1) with IPBpin (M_2) for the determination of the monomer reactivity ratios[a]

f[b]	Time, min	Conv.$_{M1}$, %[c]	Conv.$_{M2}$, %[c]	F[d]
0.097	120	10.7	9.1	0.11
0.31	60	8.0	7.0	0.34
0.50	45	9.5	10.8	0.47
0.71	30	6.2	9.2	0.62
0.90	20	5.9	18.4	0.75

[a] $[M_1 + M_2]_0/[\text{V-70}]_0$ = 1500/15 mM in DMF at 30 °C. [b] Actual monomer feed ratio ($f = [M_1]_0/([M_1]_0 + [M_2]_0)$) determined by ^{1}H NMR spectroscopy. [c] Determined by ^{1}H NMR spectroscopy. [d] Calculated from f, Conv.$_{M1}$, and Conv.$_{M2}$.

5 RAFT Copolymerization of VBaam-MOE with IPBpin

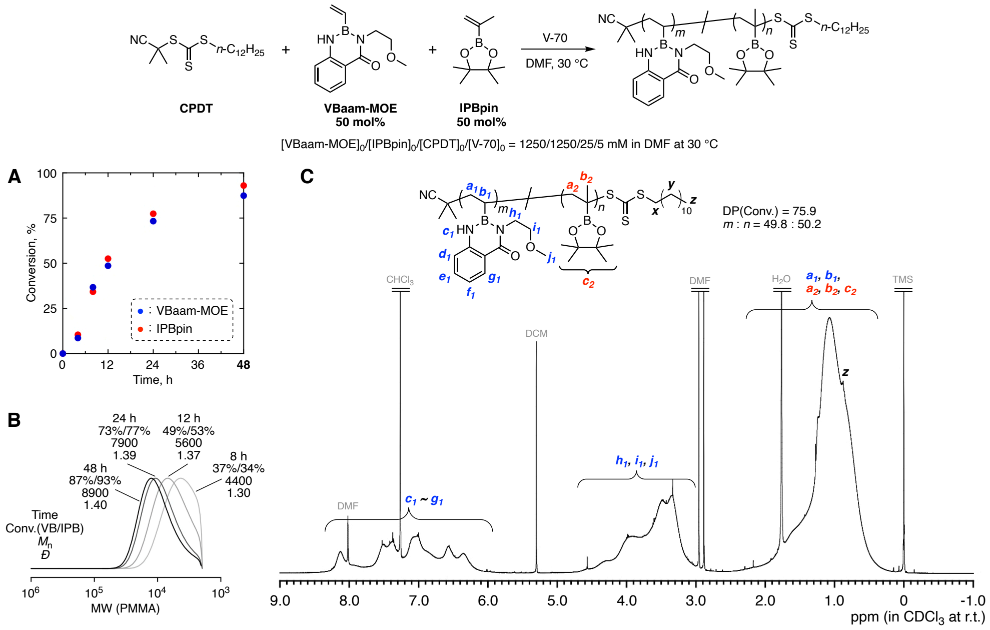


Figure S4. RAFT copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/1). (A) Time-conversion plot. (B) SEC traces for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{CPDT}]_0/[\text{V-70}]_0$ = 1250/1250/25/5 mM in DMF at 30 °C.

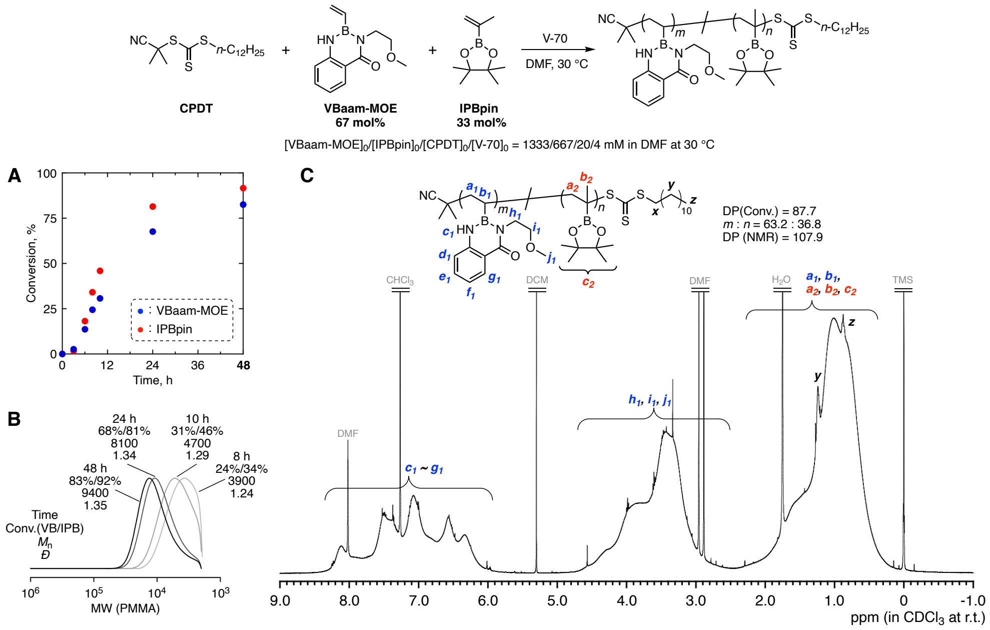


Figure S5. RAFT copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 2/1). (A) Time-conversion plot. (B) SEC traces for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{CPDT}]_0/[\text{V-70}]_0$ = 1333/667/20/4 mM in DMF at 30 °C.

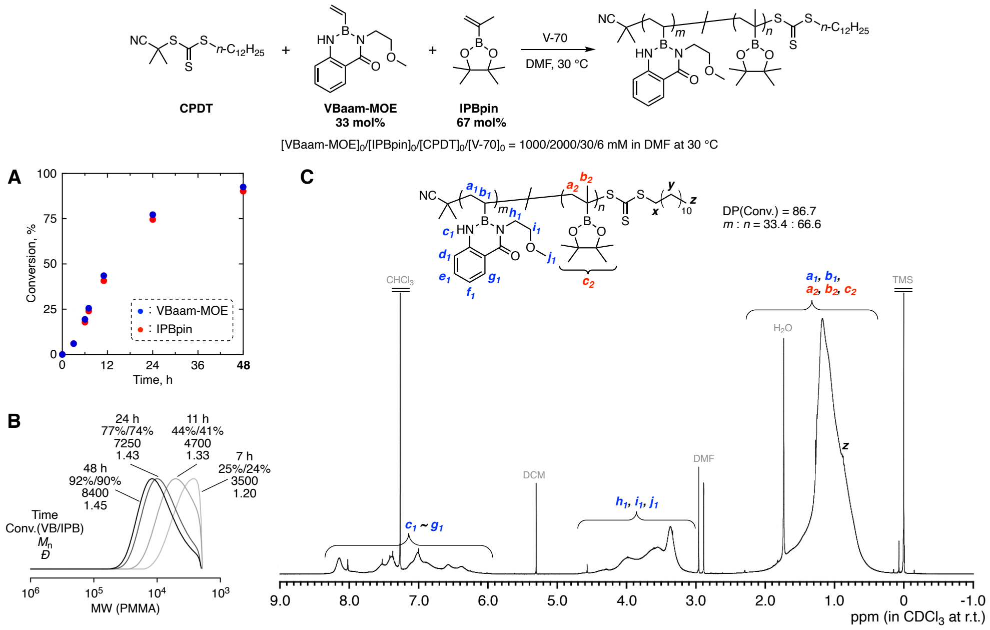


Figure S6. RAFT copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/2). (A) Time-conversion plot. (B) SEC traces for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: [VBaam-MOE]$_0$/[IPBpin]$_0$/[CPDT]$_0$/[V-70]$_0$ = 1000/2000/30/6 mM in DMF at 30 °C.

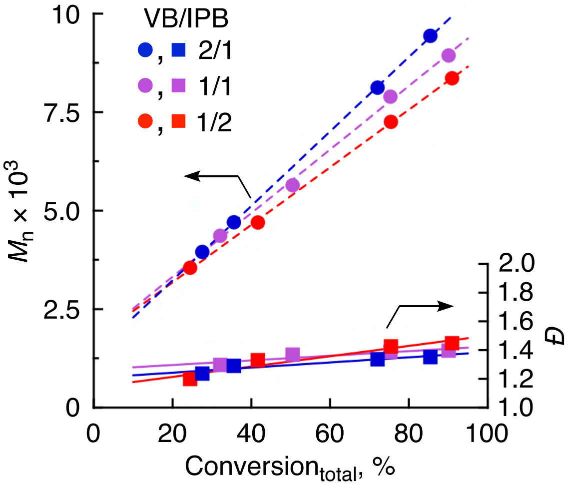


Figure S7. Conversion–M_n and conversion–$Đ$ plots for RAFT copolymerization of VBaam-MOE and IPBpin with various monomer feed ratios (blue symbols: VBaam-MOE/IPBpin = 2/1, purple symbols: VBaam-MOE/IPBpin = 1/1, red symbols: VBaam-MOE/IPBpin = 1/2).

6 Syntheses of VBaam-MOE–IPBpin (Co)polymers with Various Composition Ratios

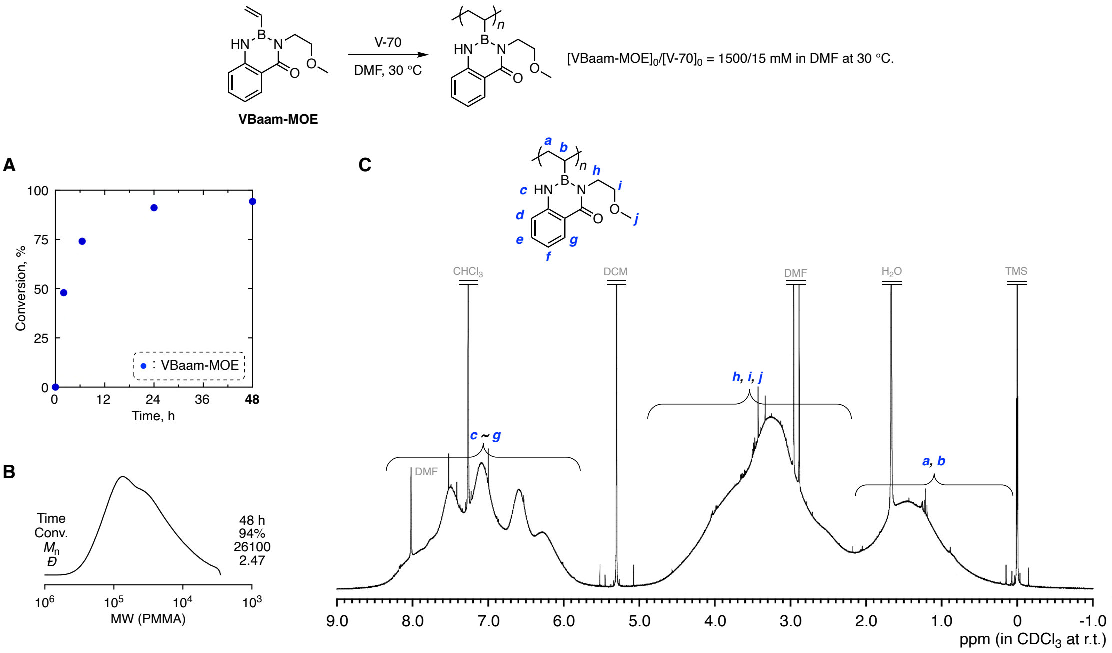


Figure S8. Free radical polymerization of VBaam-MOE. (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{V-70}]_0$ = 1500/15 mM in DMF at 30 °C.

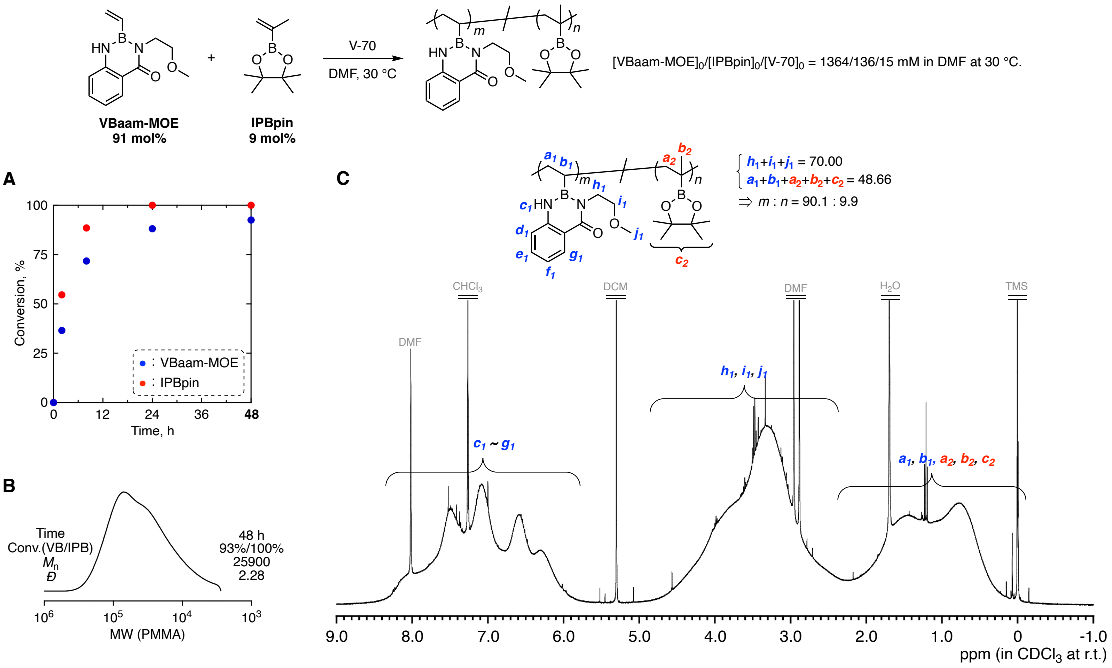


Figure S9. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 10/1). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1364/136/15 mM in DMF at 30 °C.

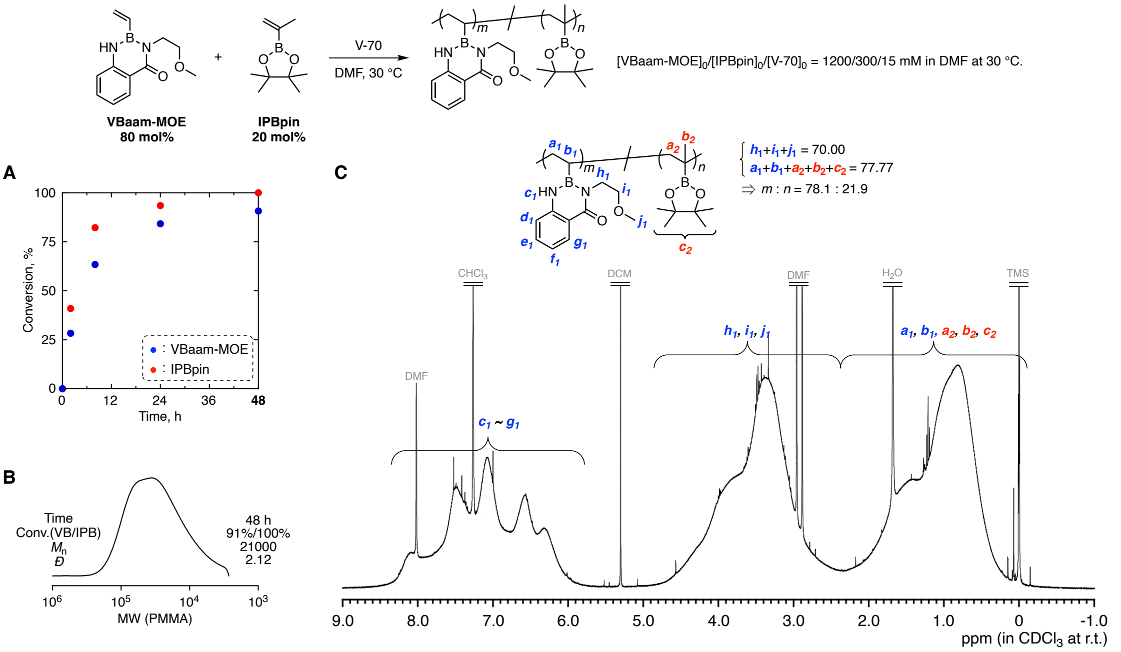


Figure S10. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 4/1). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1200/300/15 mM in DMF at 30 °C.

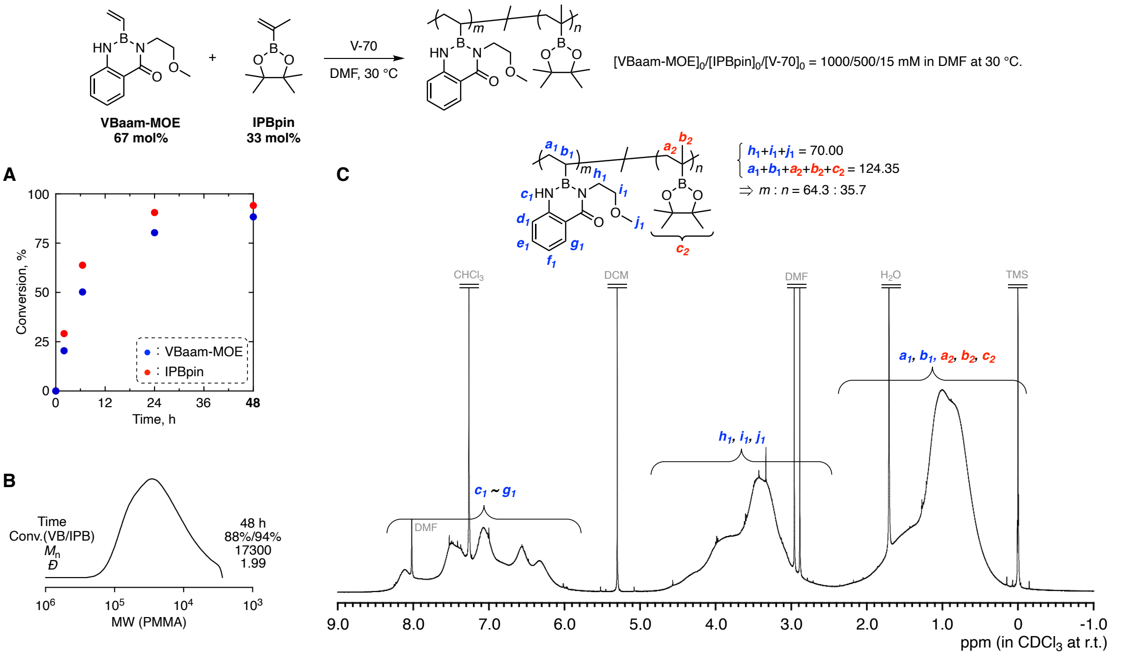


Figure S11. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 2/1). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 1000/500/15 mM in DMF at 30 °C.

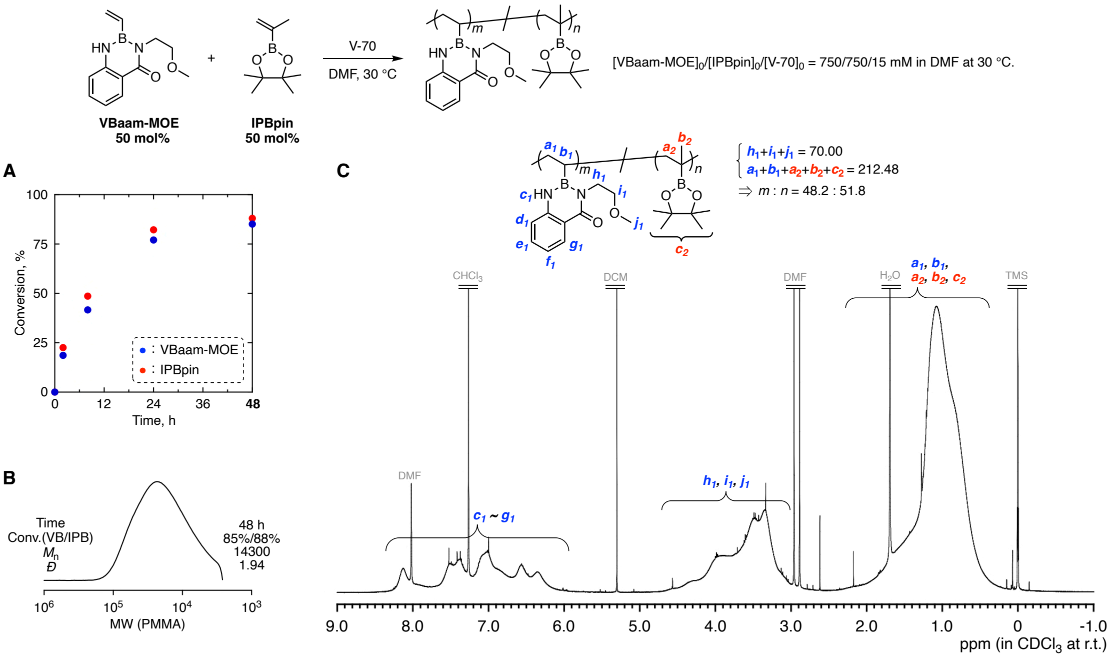


Figure S12. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/1). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 750/750/15 mM in DMF at 30 °C.

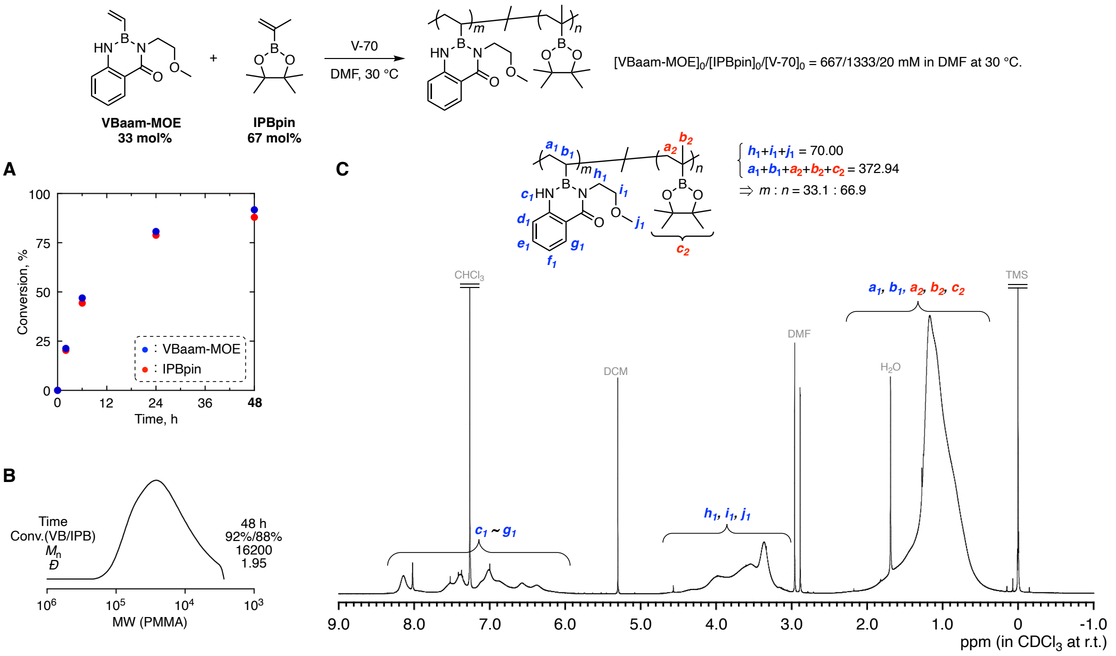


Figure S13. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/2). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[\text{VBaam-MOE}]_0/[\text{IPBpin}]_0/[\text{V-70}]_0$ = 667/1333/20 mM in DMF at 30 °C.

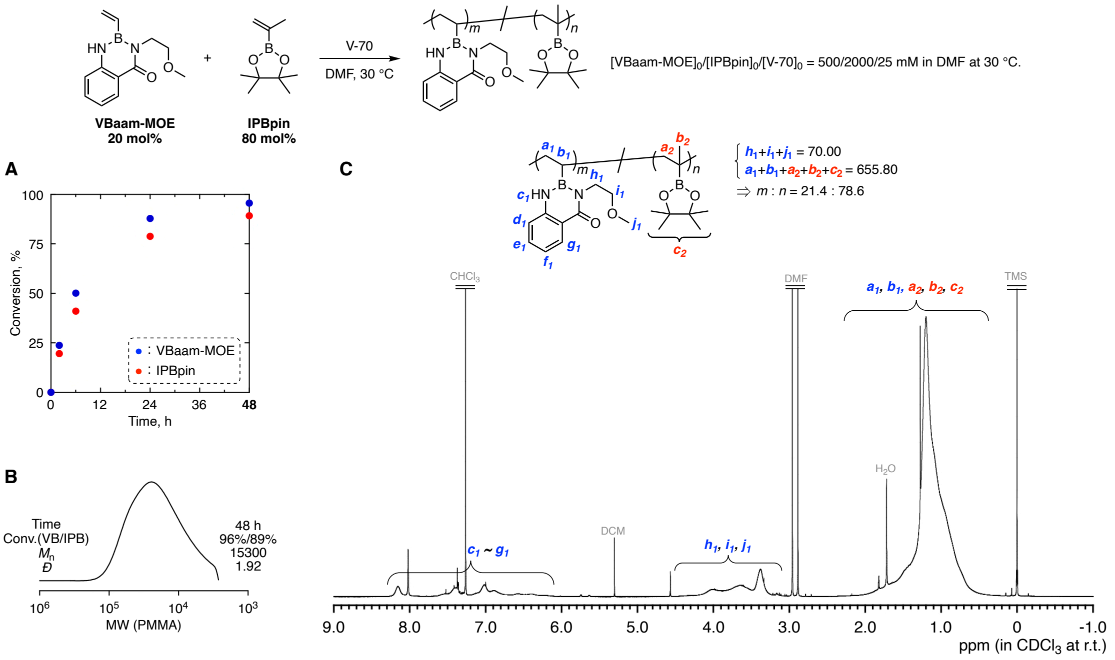


Figure S14. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/4). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in CDCl$_3$ at r.t.) of the resulting polymer. Polymerization Condition: [VBaam-MOE]$_0$/[IPBpin]$_0$/[V-70]$_0$ = 500/2000/25 mM in DMF at 30 °C.

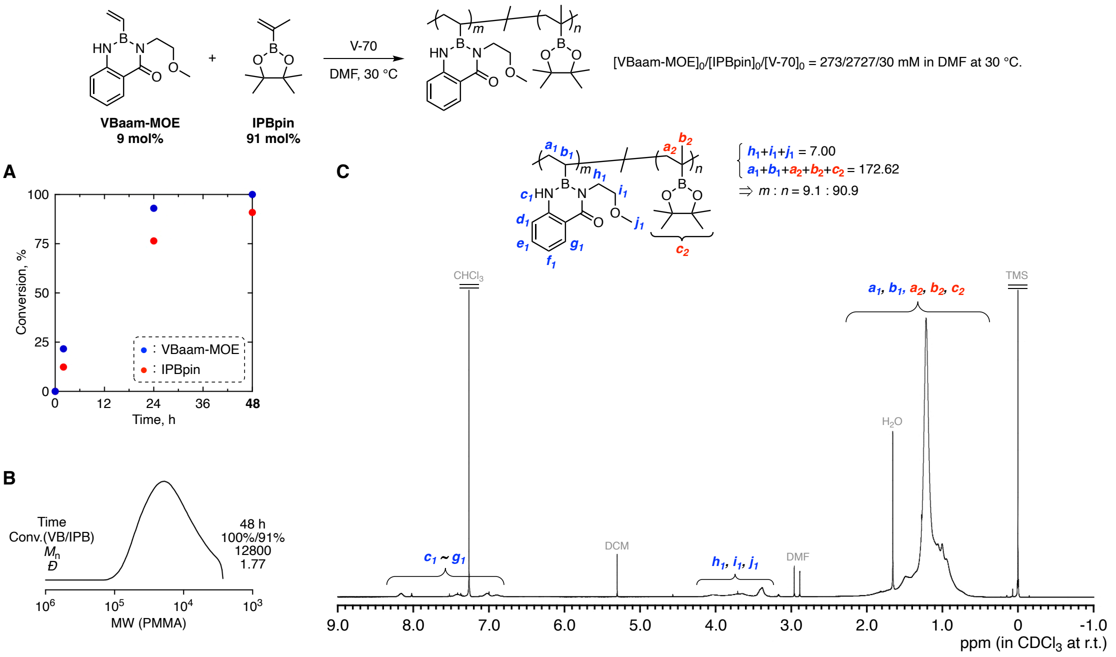


Figure S15. Free radical copolymerization of VBaam-MOE with IPBpin (VBaam-MOE/IPBpin = 1/10). (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in CDCl$_3$ at r.t.) of the resulting polymer. Polymerization Condition: [VBaam-MOE]$_0$/[IPBpin]$_0$/[V-70]$_0$ = 273/2727/30 mM in DMF at 30 °C.

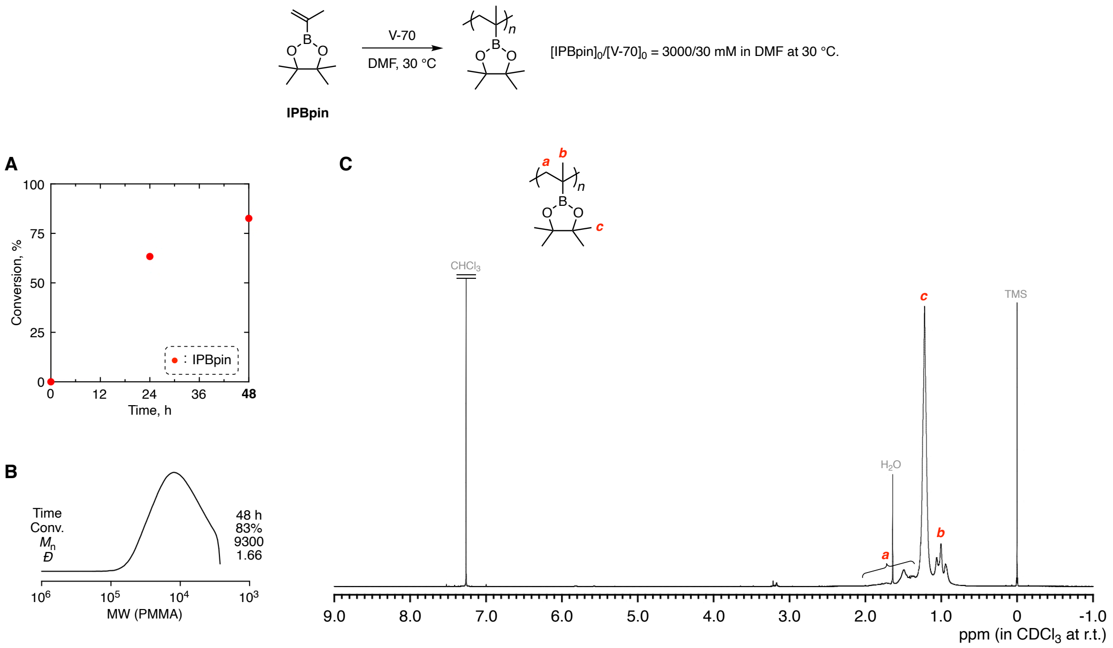
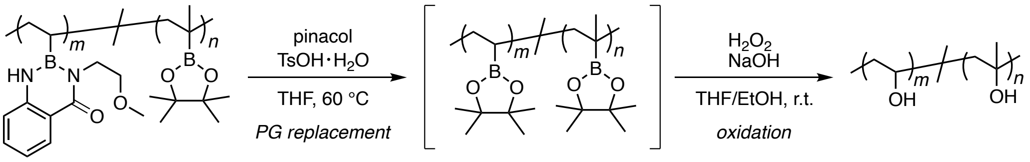


Figure S16. Free radical polymerization of IPBpin. (A) Time-conversion plot. (B) SEC trace for the polymerization. (C) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer. Polymerization Condition: $[IPBpin]_0/[V\text{-}70]_0$ = 3000/30 mM in DMF at 30 °C.

7 Syntheses of VA–IPA (Co)polymers through Side Chain Replacement

Table S3. Syntheses of VA–IPA (co)polymers through protecting group replacement and subsequent oxidation of VBaam-MOE–IPBpin (co)polymers[a]



Entry	VA/IPA target	VBaam-MOE–IPBpin (co)polymer			Protecting group (PG) replacement	VA-IPA copolymer after oxidation
		M_n[b]	$Đ$[b]	m/n[c]	Replacement rate, %[d]	m/n[c]
1	1/0	32500	2.64	100/0	85.8	100/0
2	10/1	26700	2.31	90.1/9.9	78.0	83.9/16.1
3	4/1	21000	2.04	78.1/21.9	73.7	72.8/27.2
4	2/1	17400	1.96	64.3/35.7	70.4	57.0/43.0
5	1/1	17300	1.75	48.2/51.8	74.5	45.4/54.6
6	1/2	24200	1.61	33.1/66.9	51.5	30.7/69.3
7	1/4	19900	1.68	21.4/78.6	45.0	17.6/82.4
8[e]	1/10	18300	1.54	9.1/90.9	-	7.2/92.7
9[e]	0/1	9100	1.63	0/100	-	0/100

[a] Polymerization/oxidation conditions were summarized in the experimental procedure section [b] Number-average molecular weight (M_n) and molecular weight distribution ($Đ$) of the purified (co)polymers determined by SEC with PMMA standard calibration. [c] Composition ratio of the resulting (co)polymers determined by ^{1}H NMR measurement. [d] Rate of PG replacement rate from anthranilamide to pinacol determined by ^{1}H NMR measurement. [e] PG replacement was not conducted.

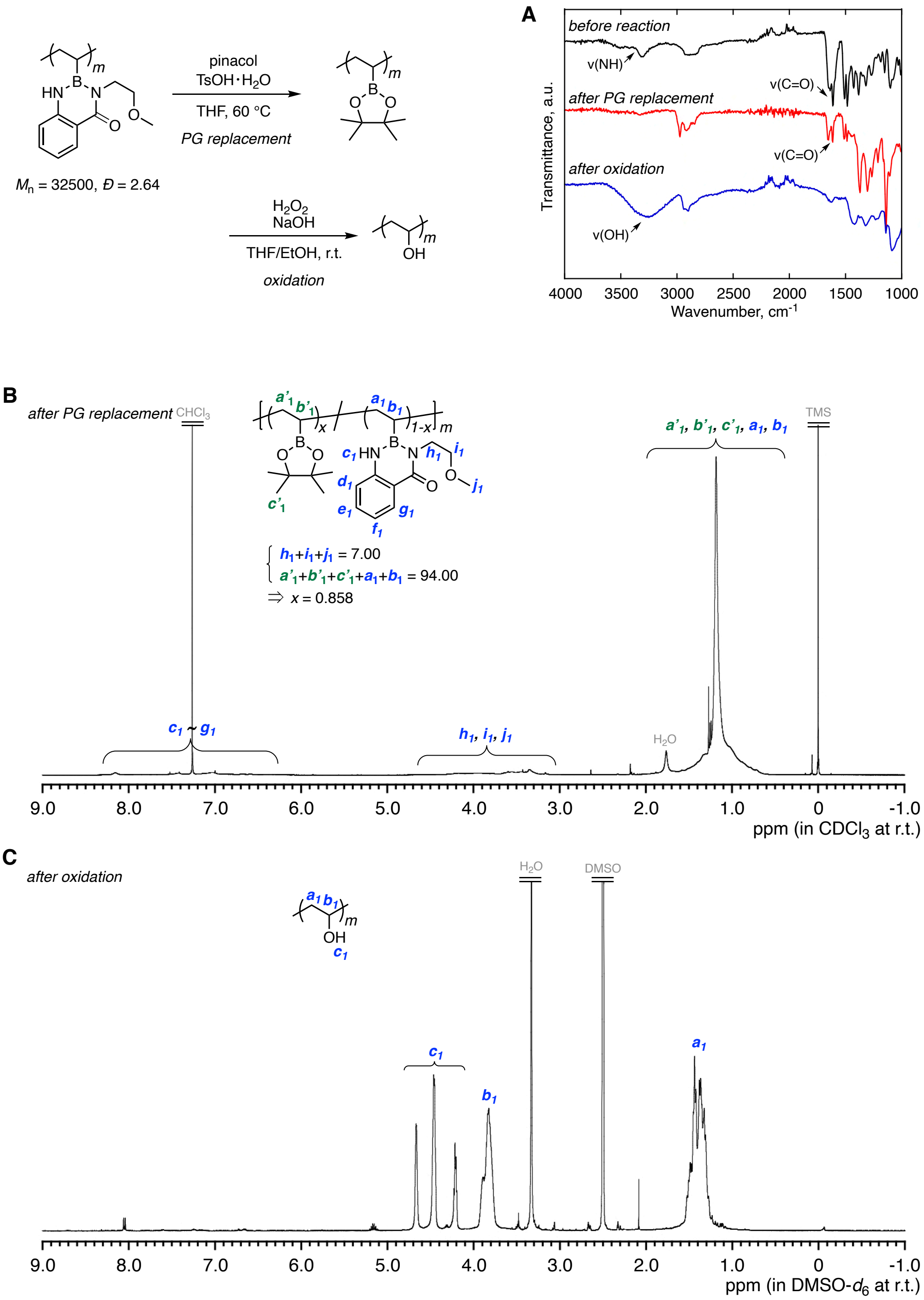


Figure S17. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE) (entry 1 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting PVA.

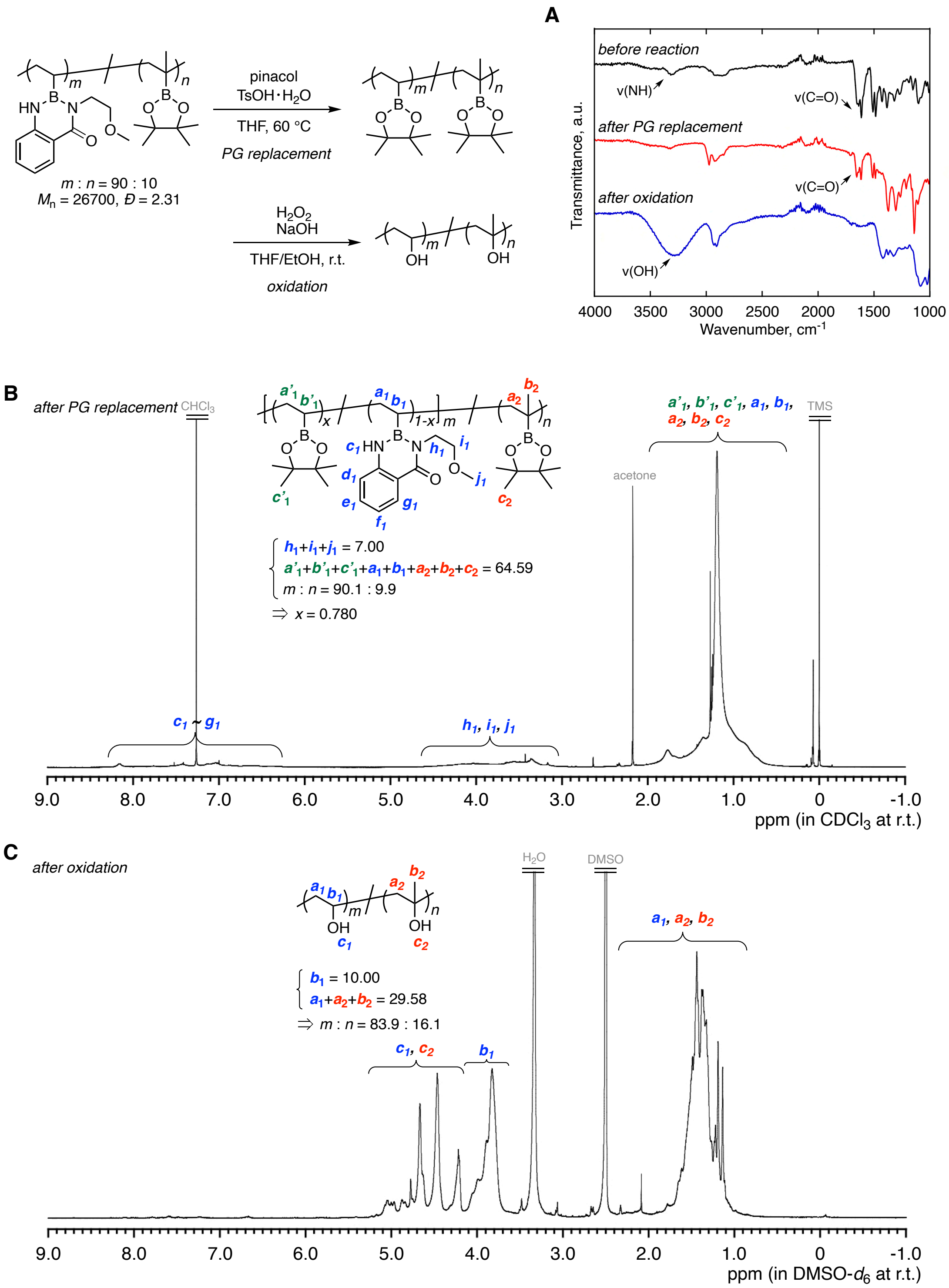


Figure S18. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 90/10) (entry 2 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

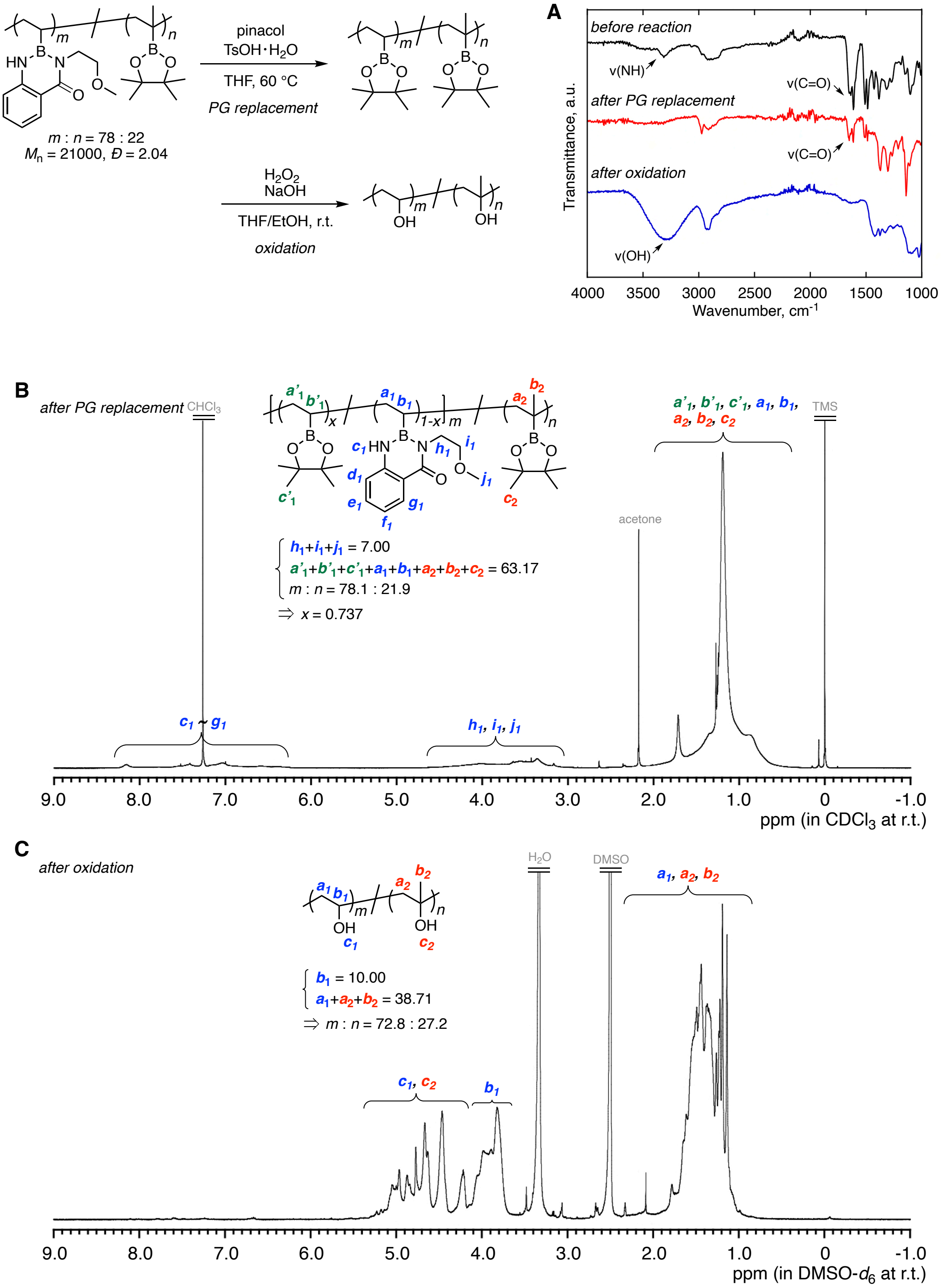


Figure S19. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 78/22) (entry 3 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

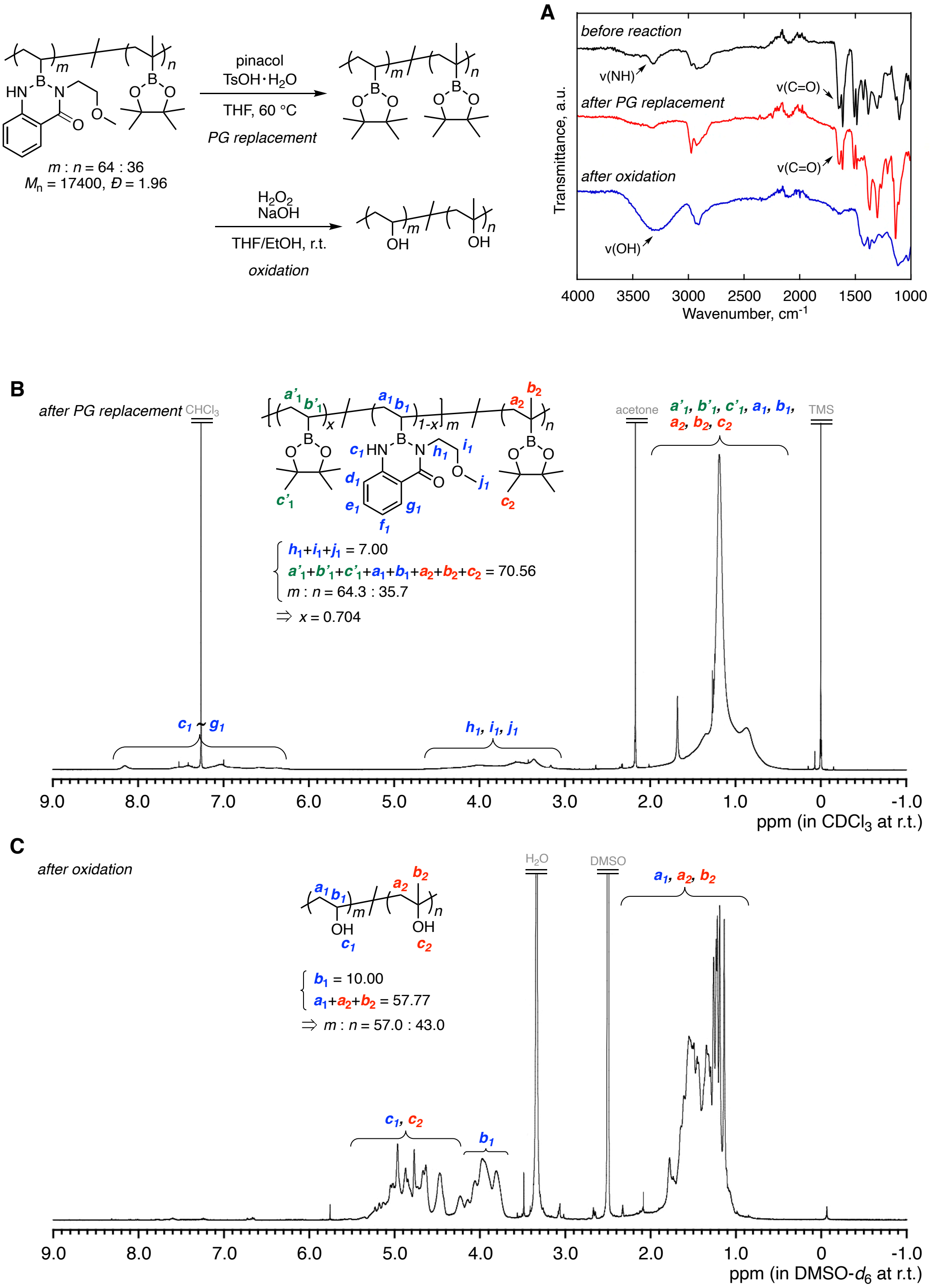


Figure S20. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 64/36) (entry 4 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

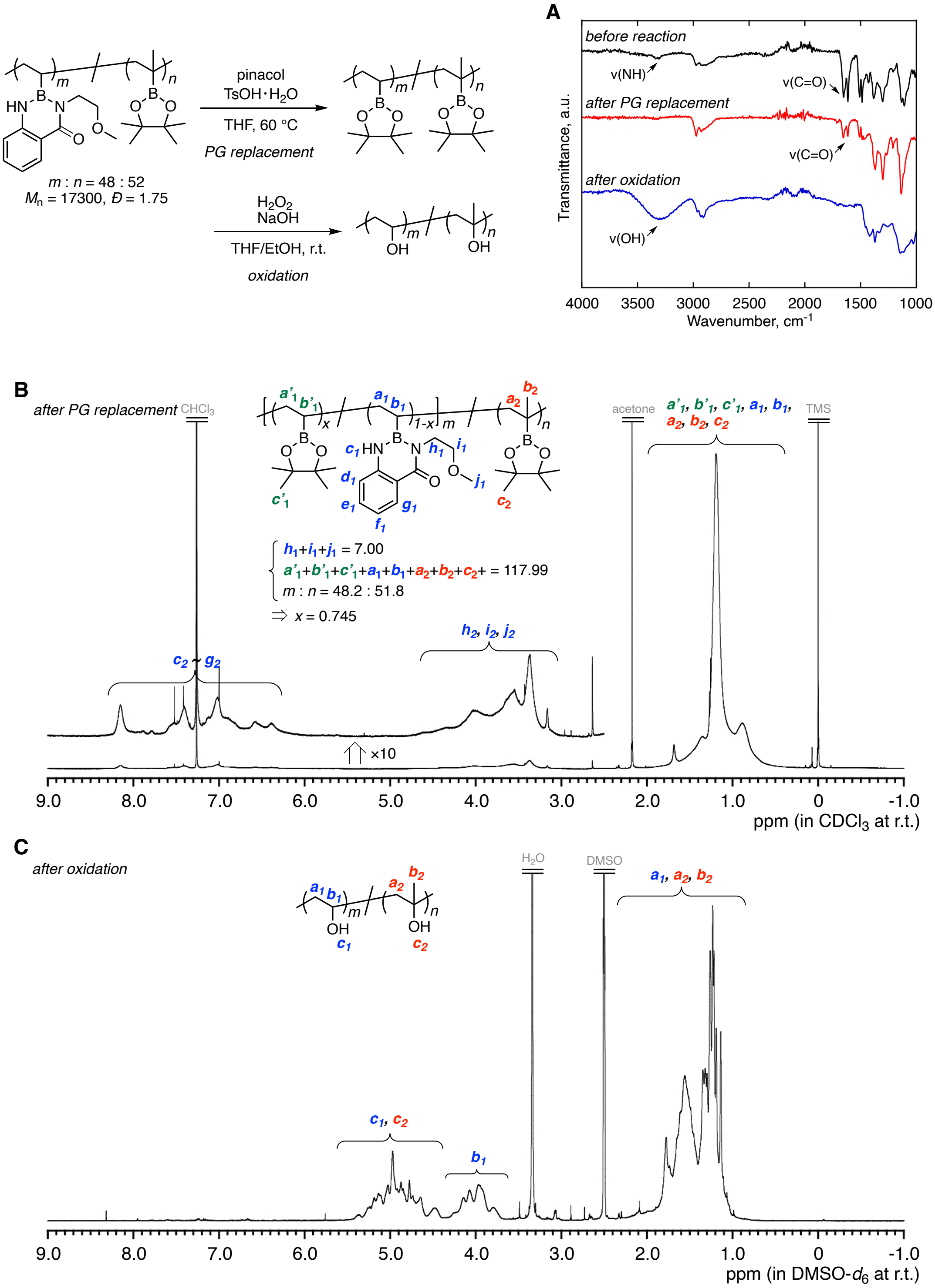


Figure S21. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 48/52) (entry 5 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^1H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^1H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

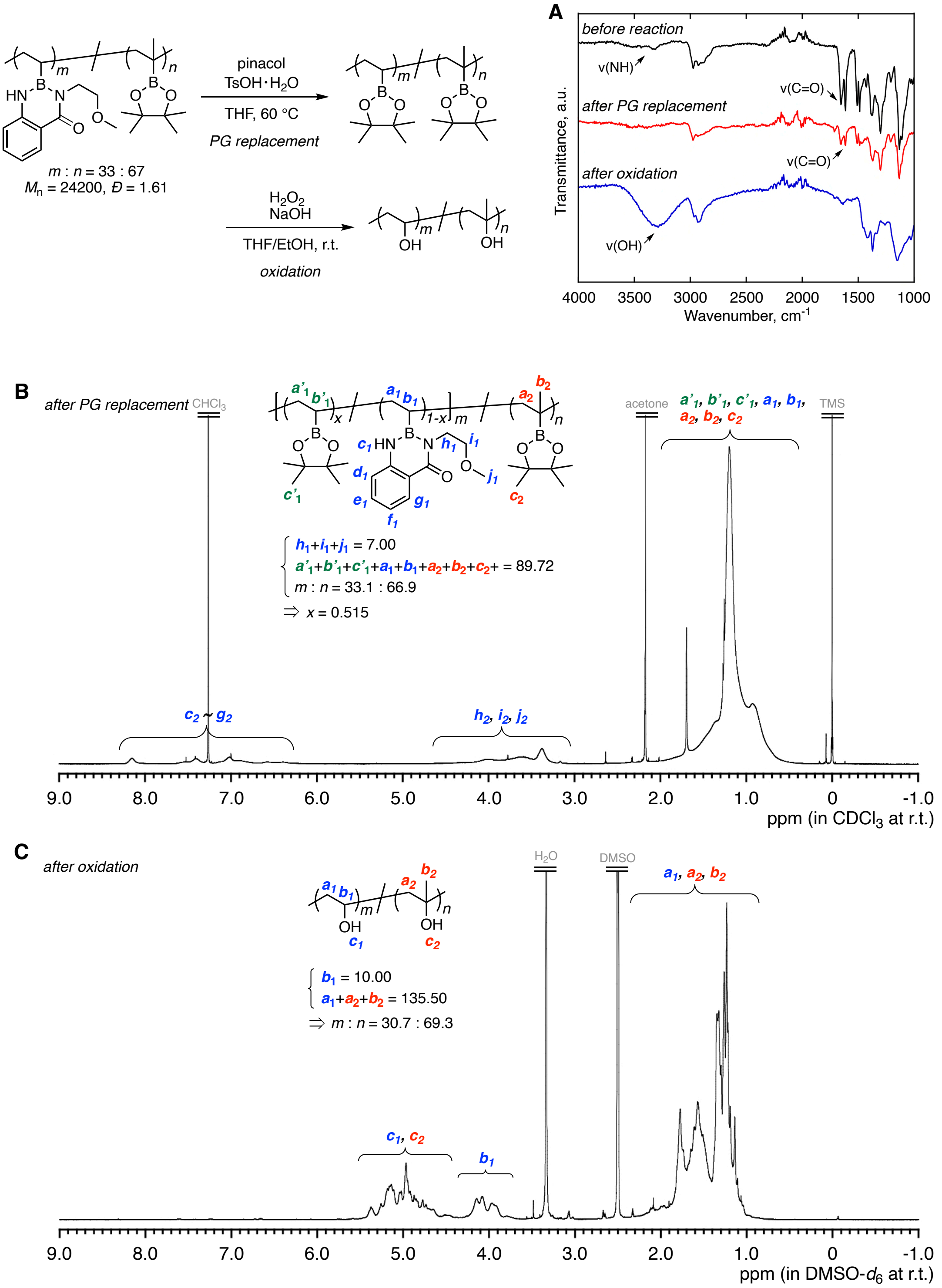


Figure S22. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 33/67) (entry 6 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

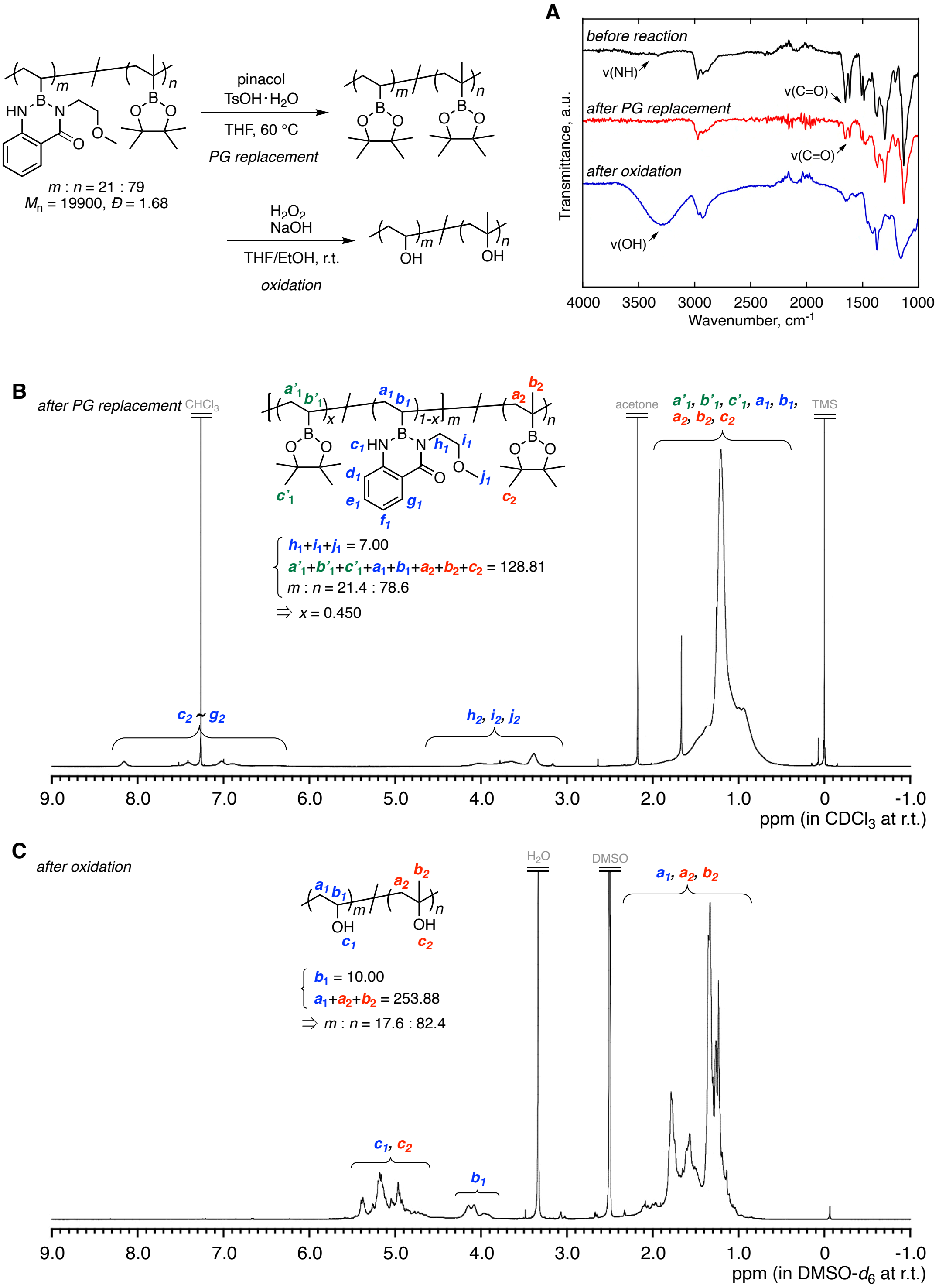


Figure S23. Protecting group replacement and subsequent oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 21/79) (entry 7 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, red line: after protecting group replacement, blue line: after oxidation). (B) ^{1}H NMR spectrum (in $CDCl_3$ at r.t.) of the resulting polymer after protecting group replacement). (C) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

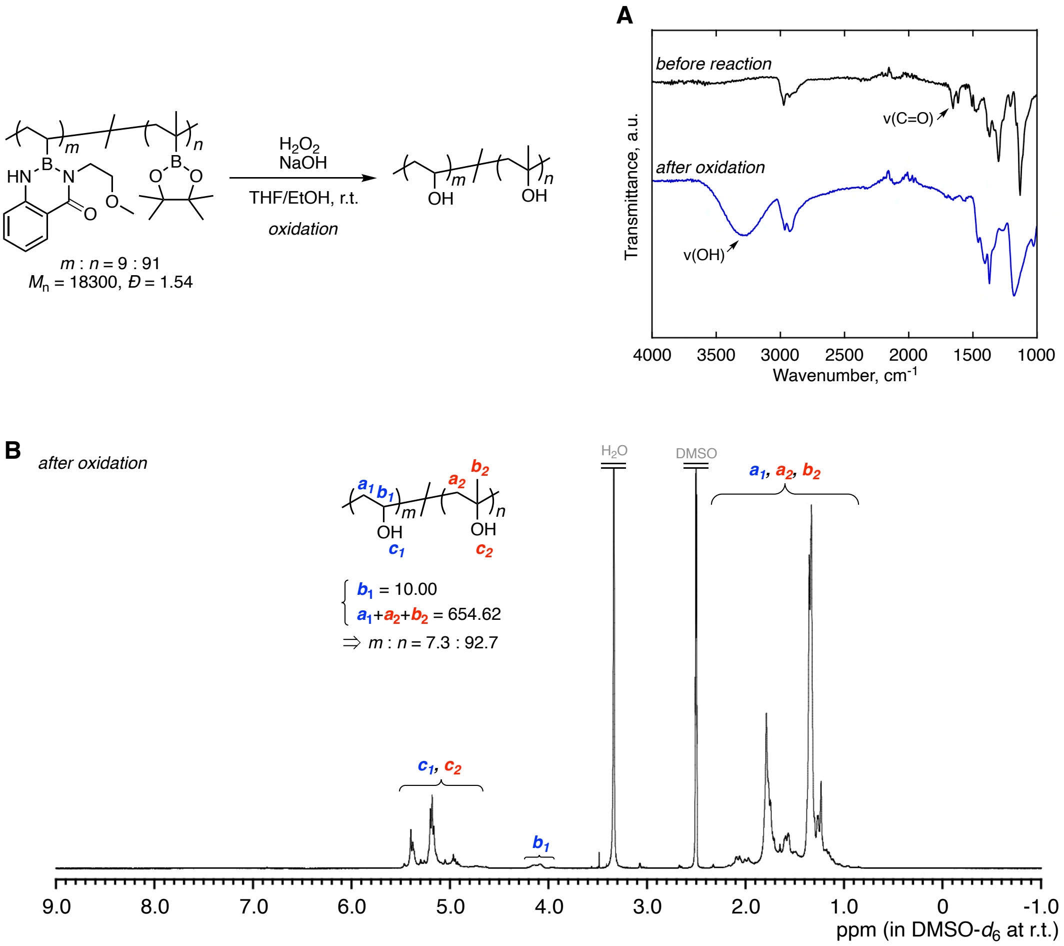


Figure S24. Oxidation of poly(VBaam-MOE-*co*-IPBpin) (VBaam-MOE/IPBpin = 9/91) (entry 8 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, blue line: after oxidation). (B) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting VA–IPA copolymer.

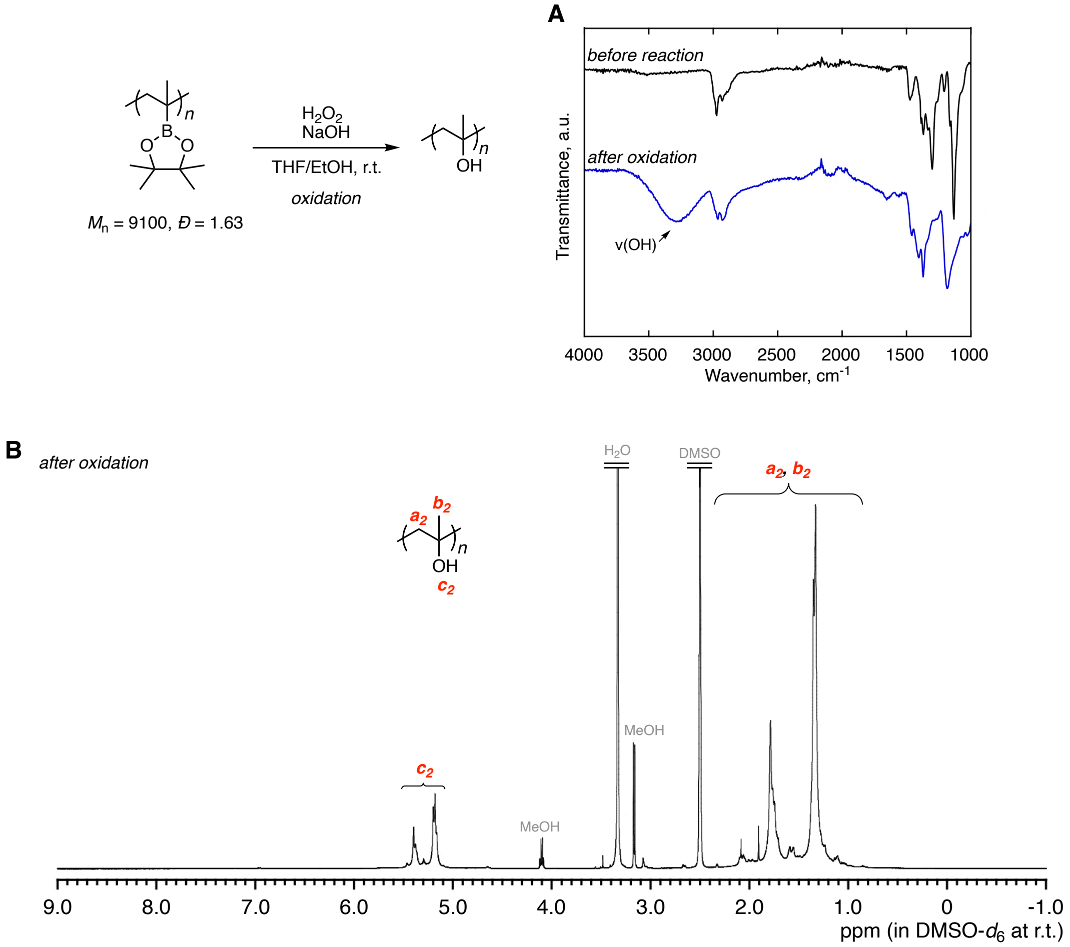


Figure S25. Oxidation of poly(IPBpin) (entry 9 in Table S3). (A) FT-IR spectra of the resulting polymers (black line: before reaction, blue line: after oxidation). (B) ^{1}H NMR spectrum (in DMSO-d_6 at r.t.) of the resulting PIPA.

8 DSC and XRD Measurements of VA–IPA (Co)polymers

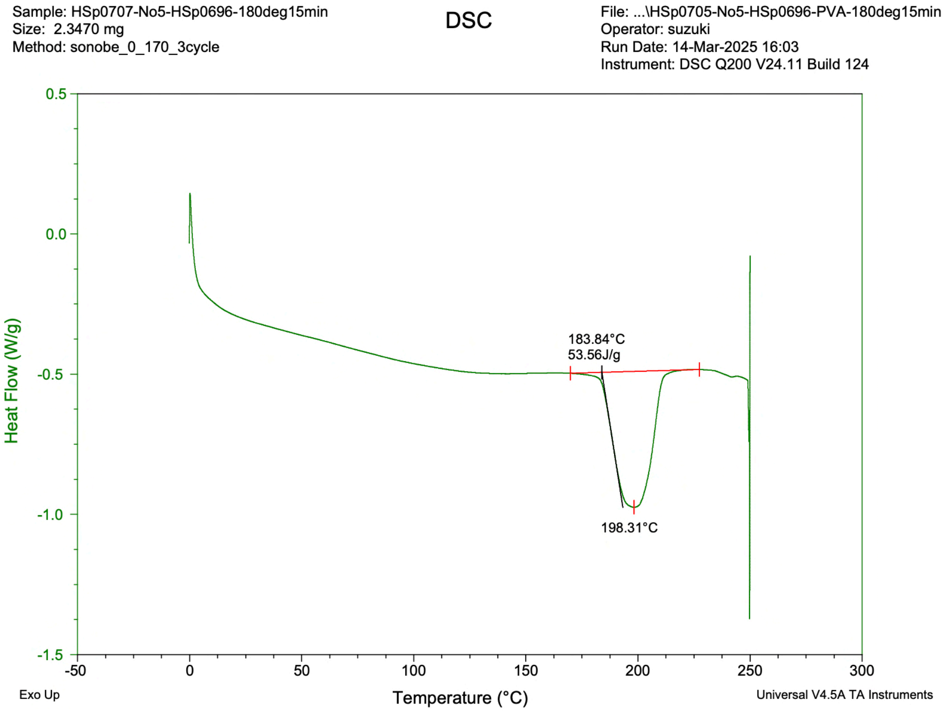


Figure S26. DSC curve of PVA (2nd heating, 10 °C/min).

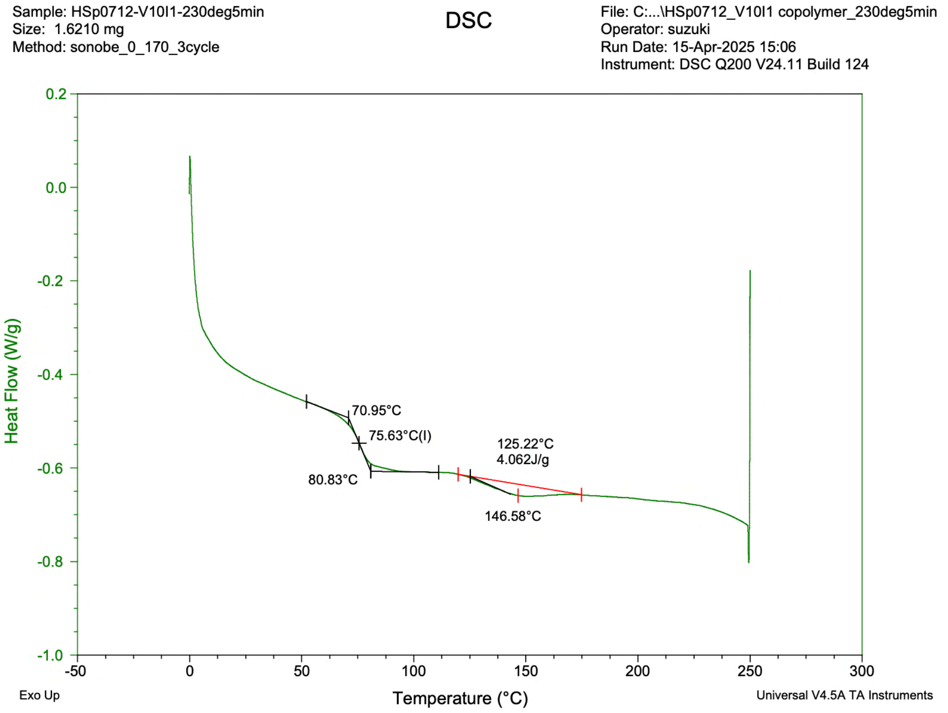


Figure S27. DSC curve of VA–IPA copolymer (VA/IPA = 84/16, 2nd heating, 10 °C/min).

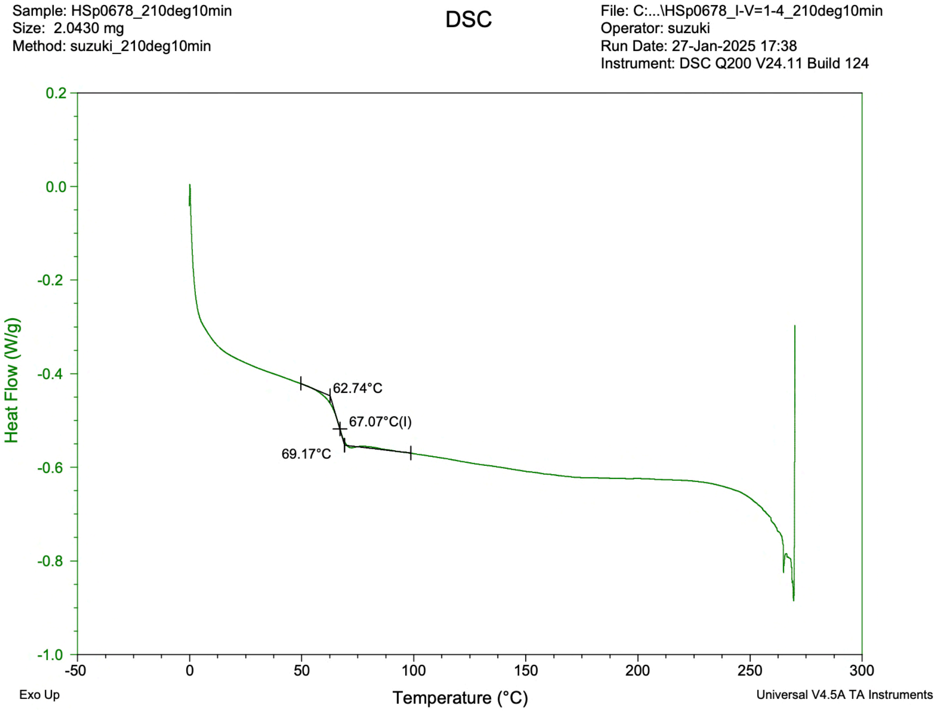


Figure S28. DSC curve of VA–IPA copolymer (VA/IPA = 73/27, 2nd heating, 10 °C/min).

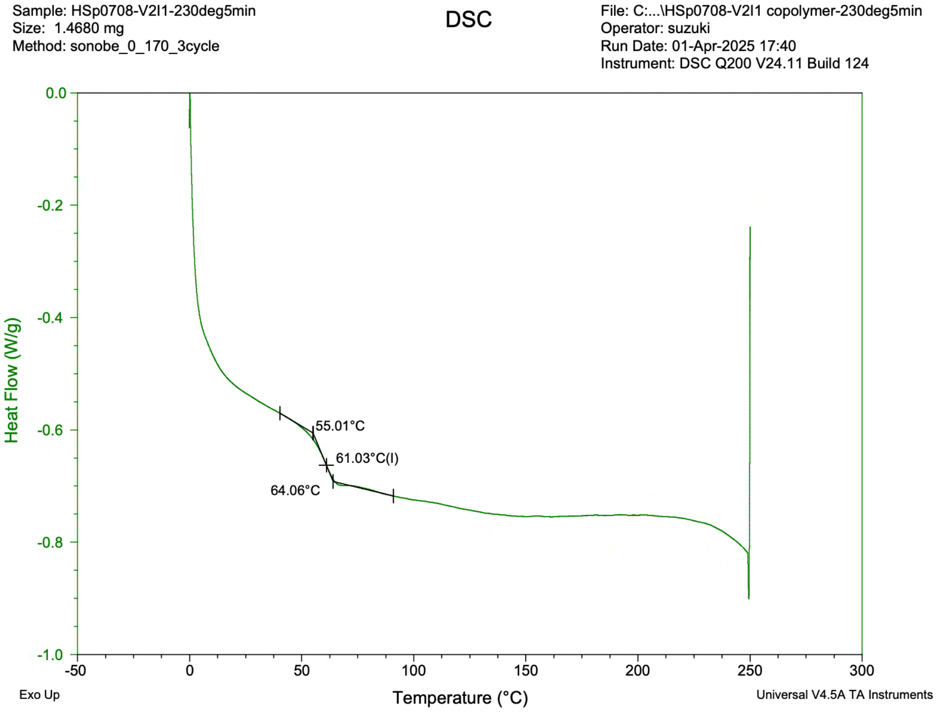


Figure S29. DSC curve of VA–IPA copolymer (VA/IPA = 57/43, 2nd heating, 10 °C/min).

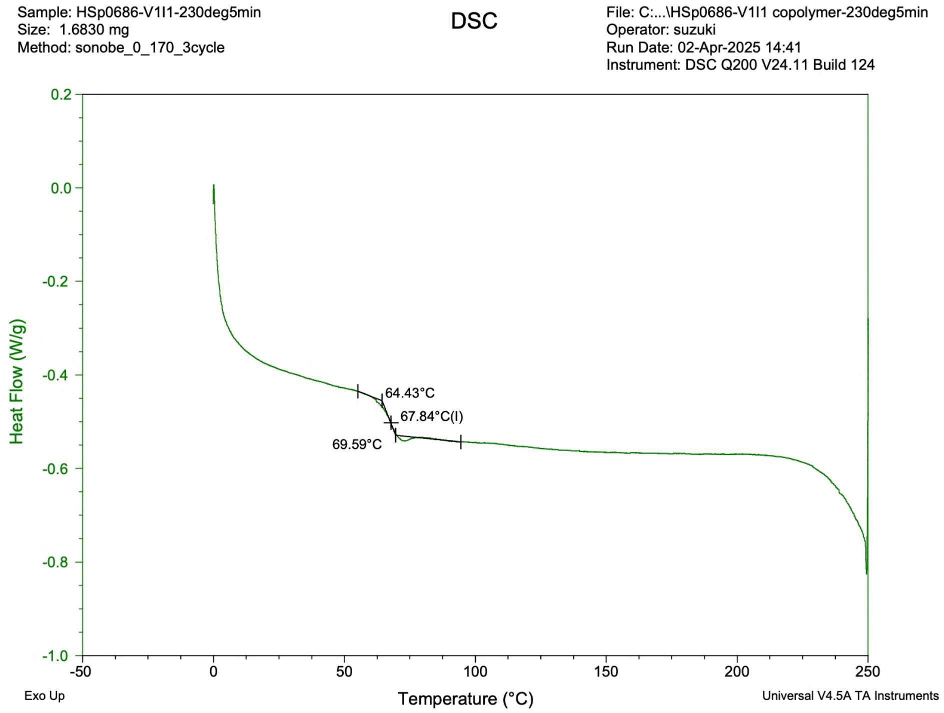


Figure S30. DSC curve of VA–IPA copolymer (VA/IPA = 45/55, 2nd heating, 10 °C/min).

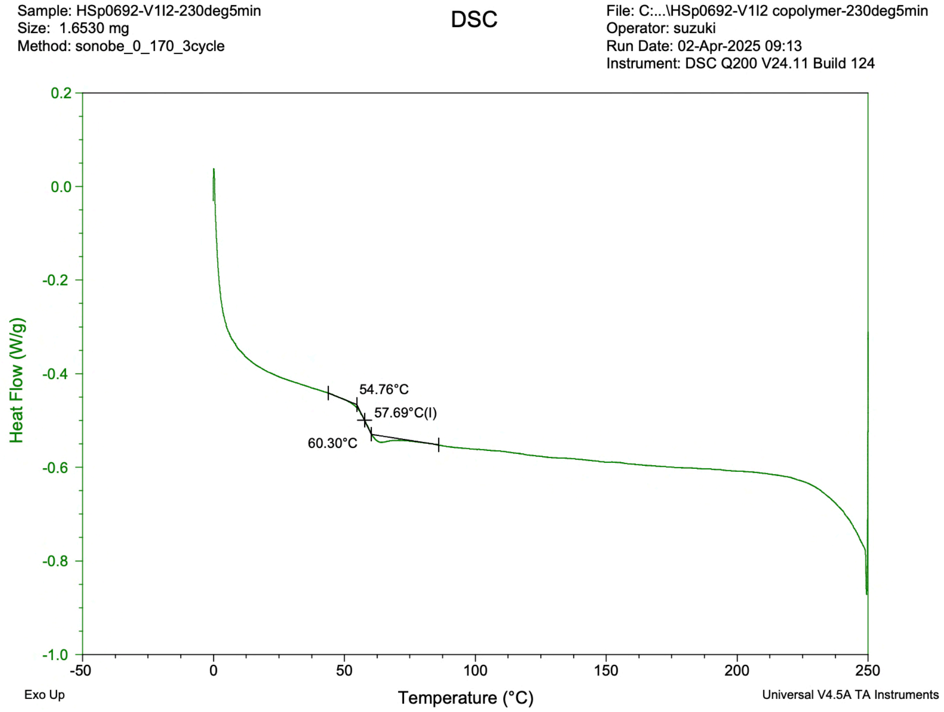


Figure S31. DSC curve of VA–IPA copolymer (VA/IPA = 31/69, 2nd heating, 10 °C/min).

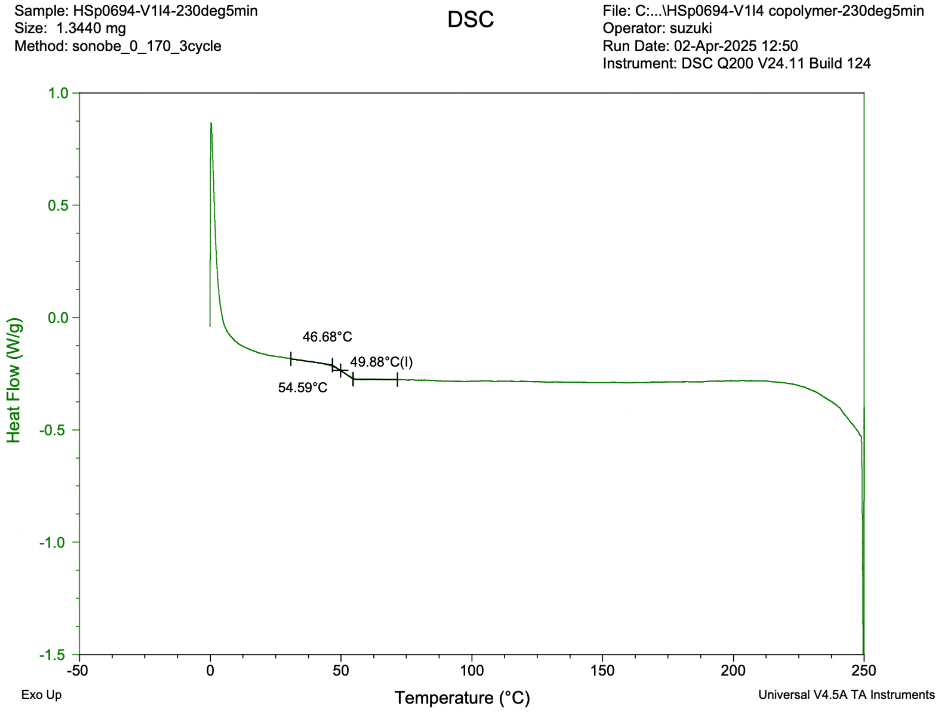


Figure S32. DSC curve of VA–IPA copolymer (VA/IPA = 18/82, 2nd heating, 10 °C/min).

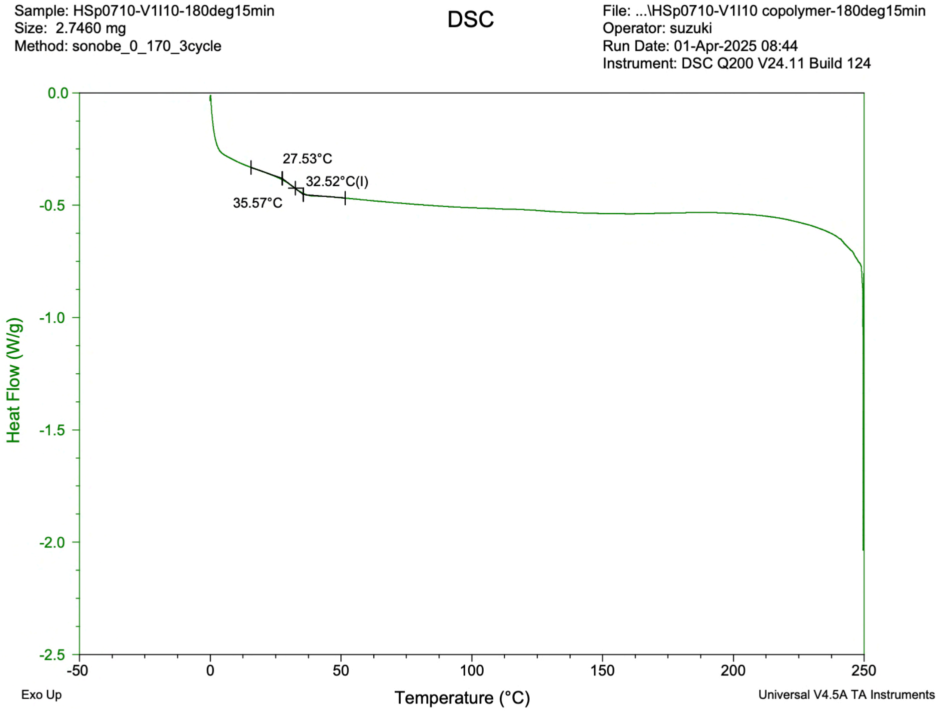


Figure S33. DSC curve of VA–IPA copolymer (VA/IPA = 7/93, 2nd heating, 10 °C/min).

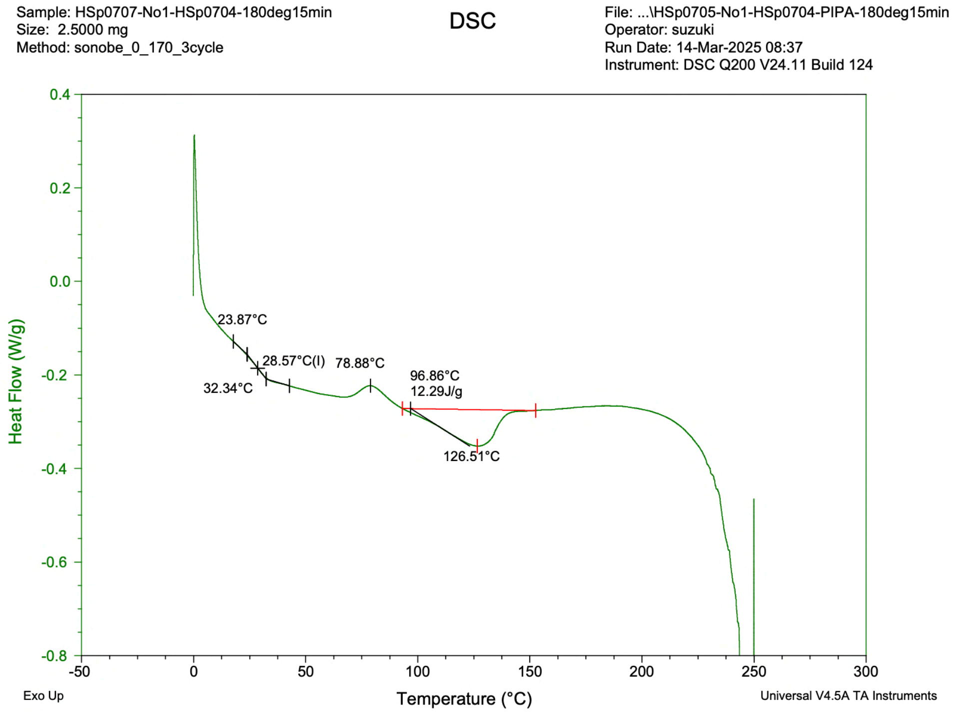


Figure S34. DSC curve of PIPA (2nd heating, 10 °C/min).

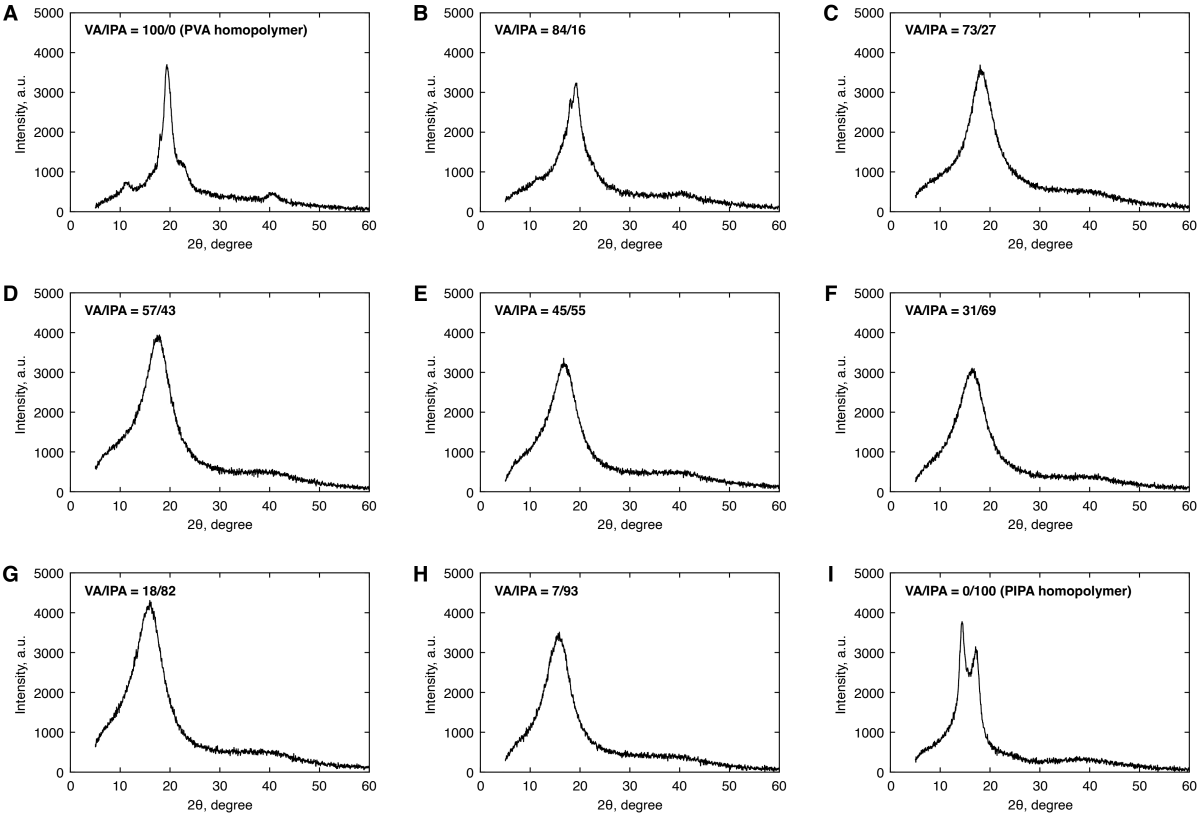


Figure S35. XRD profiles of the obtained VA–IPA (co)polymers: VA/IPA = 100/0 (A), 84/16 (B), 73/27 (C), 57/43 (D), 45/55 (E), 31/69 (F), 18/82 (G), 7/93 (H), and 0/100 (I).

Table S4. The diffraction angle (2*θ*) of the most intense peak and the calculated face distance (*d*)[a]

VA/IPA	100/0	84/16	73/27	57/43	45/55	31/69	18/82	7/93	0/100
2*θ*, degree	19.42	19.18	18.12	17.56	16.75	16.56	15.91	15.64	14.49
d, Å	4.57	4.63	4.89	5.05	5.29	5.35	5.56	5.67	6.11

[a] *d* value was calculated from the following equation: $d = \lambda/2\sin\theta$ [λ: wavelength of the incident X-ray (1.54 Å)

9 Thermal Response Behaviors of VA–IPA Copolymers in Solution States

The basic solubility of obtained VA–IPA (co)polymers (unit ratio: VA/IPA = 100/0, 84/16, 73/27, 57/43, 45/55, 31/69, 17/82, 7/93, and 0/100) were tested in the use of water, methanol, ethanol, DMF, chloroform, and acetone as the solvent. Solvent (0.5 mL) was mixed with the polymer (1.0 mg) in a glass vial, and then heated below the boiling point of the used solvent. After several hours, the content of the vial was checked visually to judge the solubility.

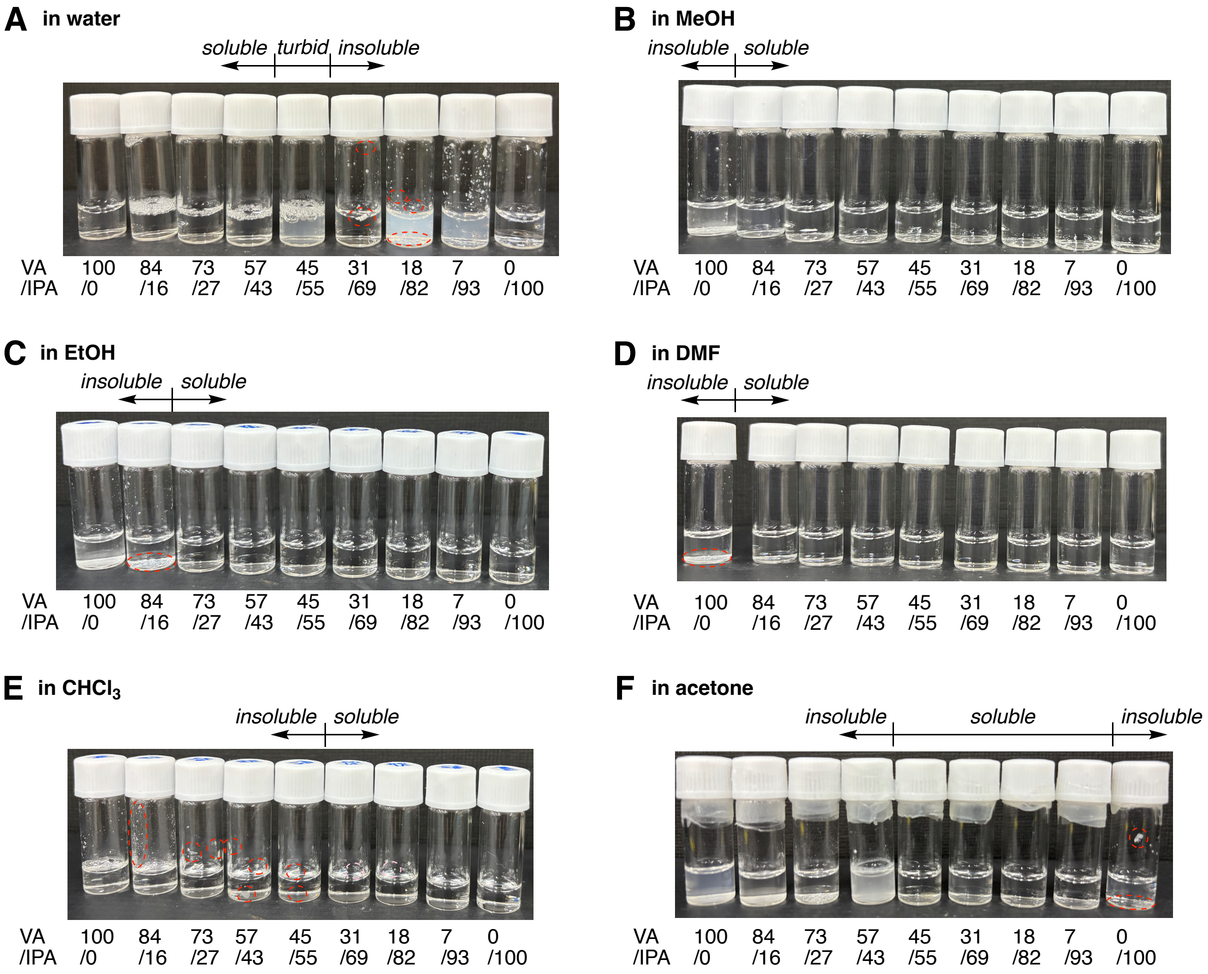


Figure S36. Photos for solubility tests of VA–IPA (co)polymers in water (A), MeOH (B), EtOH (C), DMF (D), $CHCl_3$ (E), and acetone (F) (2 mg/mL).

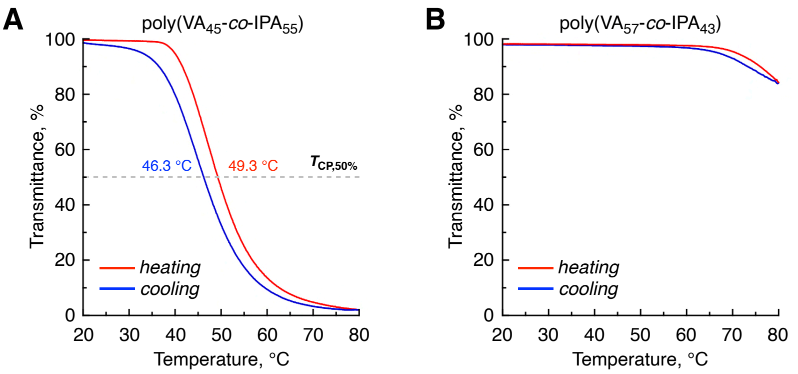


Figure S37. Temperature-variable transmittance measurement by UV-vis ($\lambda = 670$ nm) on the heating (red line) and cooling (blue line) process (1 °C min^{-1}) of the aqueous solutions of VA–IPA copolymer [VA/IPA = 45/55 (A) and 57/43 (B), 2 mg mL^{-1}]

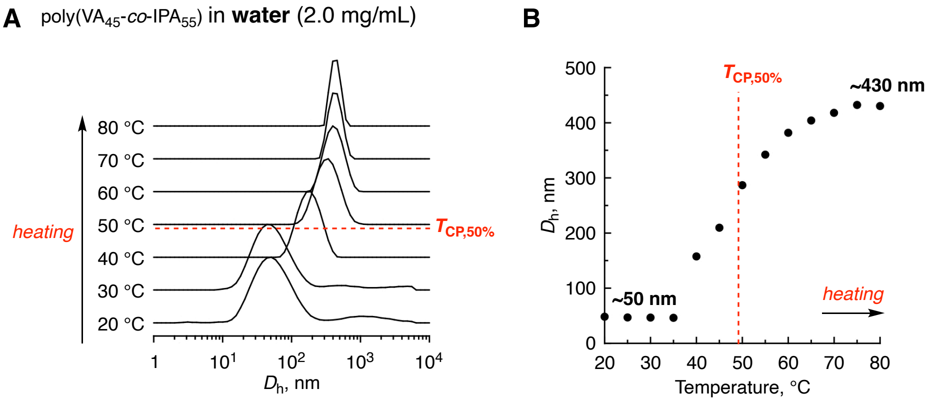


Figure S38. (A) DLS charts of aqueous solution of VA–IPA copolymer (VA/IPA = 45/55) (2.0 mg/mL) in heating process from 20 °C to 80 °C. $T_{CP,\ 50\%}$ indicates the temperature at which the transmittance reached 50%. (B) Temperature–averaged hydrodynamic diameter (D_h) plots.

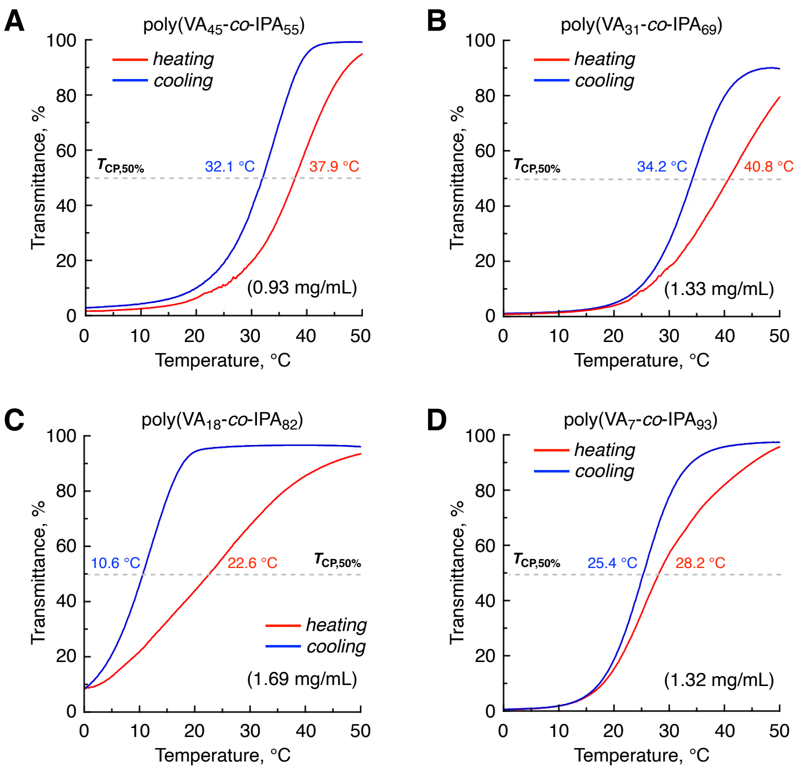


Figure S39. Temperature-variable transmittance measurement by UV-vis ($\lambda = 670$ nm) on the heating (red line) and cooling (blue line) process (1 °C min^{-1}) of the saturated acetone solutions of VA–IPA copolymer [VA/IPA = 45/55 (A), 31/69 (B), 18/82 (C), and 7/93 (D)]. The polymer concentration was determined by measuring the weight of the residual polymer after evaporating the solution of 150 μL.

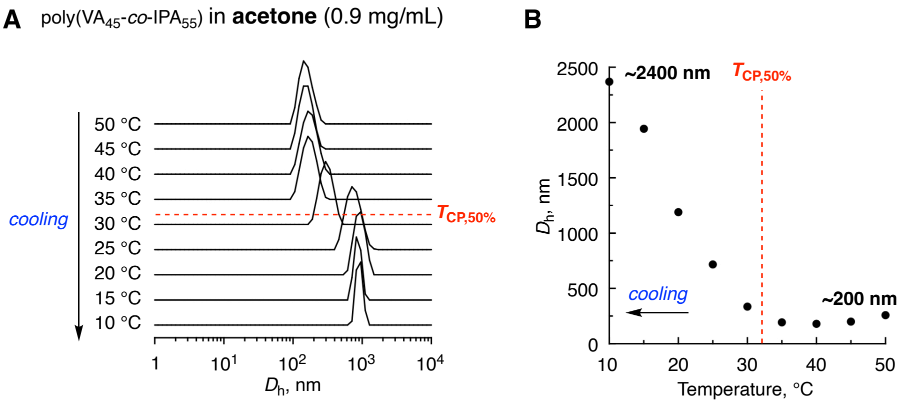


Figure S40. (A) DLS charts of acetone solution of VA–IPA copolymer (VA/IPA = 45/55) (0.9 mg/mL) in cooling process from 50 °C to 10 °C. $T_{\mathrm{CP,\,50\%}}$ indicates the temperature at which the transmittance reached 50%. (B) Temperature–averaged hydrodynamic diameter (D_h) plots.

10 References

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