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Supporting Information

Self-healing amino acid-bearing acrylamides/*n*-butyl acrylate copolymers via multiple noncovalent bonds

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Experimental Section

Materials.

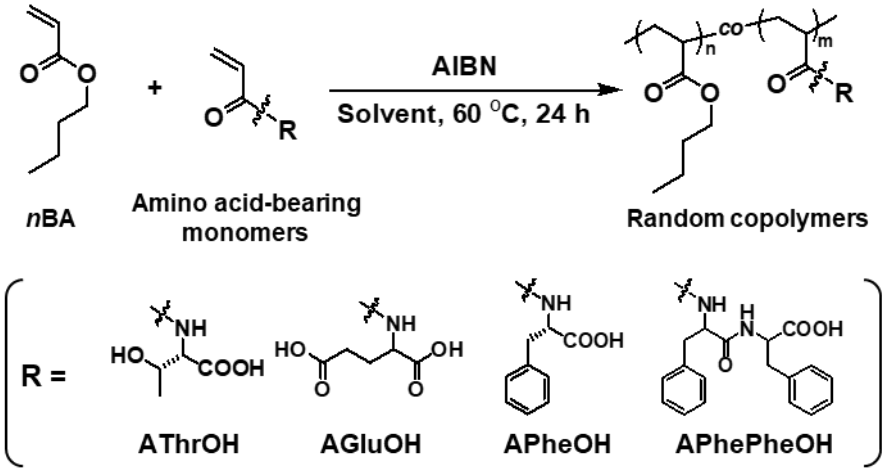
2,2'-Azobis(isobutyronitrile) (AIBN, 97 %) was purchased from Kanto Chemical, and recrystallized from methanol. *n*-Butyl acrylate (*n*BA, >99 %) was purchased from Aldrich and purified by vacuum distillation. *N*-Acryloyl-L-threonine (AThrOH),[2,3] *N*-acryloyl-L-glutamic acid (AGluOH),[4,5] *N*-acryloyl-L-phenylalanine (APheOH),[6] and *N*-acryloyl-L,L-diphenylalanine (APhePheOH)[7] were synthesized as previously reported with slight modifications. 2-Cyano-2-propyl dodecyl trithiocarbonate (Aldrich, >97%) was used as received. Benzyl 1-pyrrolecarbodithioate was synthesized as previously reported.[8,9]

Synthesis of *N*-acryloyl-L-glutamic acid (AGluOH)

A representative monomer synthesis is as follows. Acryloyl chloride (6.9 mL, 85.0 mmol) was added dropwise to 25 wt.% NaOH aqueous solution (100 mL) of L-glutamic acid (12.5 g, 85.0 mmol) under nitrogen, which was maintained at 0 °C by cooling with an external ice bath. After the complete addition of L-glutamic acid, the mixture was stirred for overnight while the temperature was allowed to rise to room temperature. The mixture was acidified to pH 2-3 with 1 N HCl. After saturation of the solution with NaCl (5.00 g), ethyl acetate was employed to extract the product three time. The extract was then dried over anhydrous $MgSO_4$, filtered, and the solvent evaporated. The crude product was purified by recrystallization from methanol-ethyl acetate/hexane. After filtration, the product was finally dried under vacuum at room temperature to afford A-Glu-OH as a white solid, yield: 6.1 g (yield = 35 %). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.47 (s, 2H: -COO*H*), 8.40 (d, 1H: -N*H*), 6.30 (q, 1H: -C*H*=CH_2), 6.12 (dd, 1H: -CH=CH_2), 5.64 (dd, 1H: -CH=CH_2), 4.29 (q, 1H: -NH-C*H*), 2.29 (t, 2H: -CH_2-COOH), 2.00 (q, 1H: -CH_2-), 1.79 (q, 1H: -CH_2-) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ

173.80 (-*C*OOH), 165.16 (-*C*O-NH-), 131.25 (-*C*H=CH_2), 125.93 (-CH=*C*H_2), 51.71 (-NH-*C*H), 30.56 (-*C*H_2), 26.85 (-*C*H_2) ppm.

Polymer Synthesis.



Scheme S1. Synthesis of amino acid-based copolymers.

Synthesis of P(*n*BA-*co*-AGluOH)

For the synthesis of a representative P(*n*BA-*co*-AGluOH) (Run 7 in Table S1), AGluOH (422.5 mg, 2.1 mmol), *n*BA (808 mg, 6.3 mmol), AIBN (7.00 mg, 0.042 mmol), and dry EtOH (4.01 mL) were added in a dry polymerization ampule equipped with a magnetic stir bar. After degassing the mixture by three freeze-evacuate-thaw cycles, the glass ampule was flame-sealed under vacuum. The mixture was stirred at 60 °C for 24 h. Subsequently, the reaction mixture was poured into a large excess of *n*-hexane and purified by decantation. After the residue was dissolved in ethanol, followed by evaporation, the product was finally dried in vacuo at 60 °C overnight to yield P(*n*BA-*co*-AGluOH) as a semi-transparent solid (yield = 95 %, 1.16 g). The chemical structure and comonomer composition were verified via ^{1}H NMR (Figures S2 and S3) spectroscopy.

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.46 (broad, 2H: -COO*H*), 7.38-8.35 (broad, 1H: -N*H*), 3.74-4.48 (broad, 3H: -O-CH_2- in *n*BA, -NH-C*H* in AGluOH), 2.04-2.44 (broad, 3H: -C*H* (main chain) in *n*BA,

-C*H*$_2$-COOH), 1.86-2.03 (broad, 2H: -C*H*$_2$- in AGluOH), 1.52 (broad, 2H: -C*H*$_2$- in *n*BA), 1.31 (broad, 2H: -C*H*$_2$-CH$_3$), 0.88 (broad, 3H: -CH$_2$-C*H*$_3$), 1.08-2.05 (broad, C*H* and C*H*$_2$ in the main polymer chain) ppm.

The molecular weight and dispersity were verified by SEC measurement of the methylated sample (Figure S7) prepared by treating P(*n*BA-*co*-AGluOH) with trimethylsilyldiazomethane, as previously reported.[6,10] It must be noted that trimethylsilyldiazomethane should be regarded extremely toxic, and all of its handling and the evaporation process should be conducted with proper ventilation.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-8.25 (broad, 1H: -N*H*), 3.55-4.74 (broad, 3H: -O-C*H*$_2$- in *n*BA, -NH-C*H* in AGluOMe), 3.67 (broad, 6H: -O-C*H*$_3$ in AGluOMe), 2.31-2.58 (broad, 3H: -C*H* (main chain) in *n*BA, -C*H*$_2$-COOCH$_3$, 2.06-2.31 (broad, 2H: -C*H*$_2$- in AGluOMe), 1.60 (broad, 2H: -C*H*$_2$- in *n*BA), 1.14-1.41 (broad, 2H: -C*H*$_2$-CH$_3$), 0.91 (broad, 3H: -CH$_2$-C*H*$_3$), 1.10-2.06 (broad, C*H* and C*H*$_2$ in the main polymer chain) ppm.

The copolymer composition of P(*n*BA-*co*-AGluOH) was determined by comparison of the ^{1}H NMR peaks corresponding to the comonomers of the methylated sample using the equation (S1)

$$\frac{3x}{6(1-x)} = \frac{Integral\ at\ 0.91\ ppm}{Integral\ at\ 3.67\ ppm} \quad \text{(S1)}$$

where *x* is the fraction of the *n*BA and 1-*x* is the fraction of AGluOMe in the random copolymer. The peaks at 0.91 ppm correspond to methyl protons of *n*BA unit (3H), while the peak at 3.67 ppm corresponds to methyl protons of AGluOMe (6H).

Synthesis of P(*n*BA-*co*-AThrOH)

P(*n*BA-*co*-AThrOH)s were synthesized using the same copolymerization and purification procedures employed for the synthesis of P(*n*BA-*co*-AGluOH). The chemical structure and comonomer

composition were verified via ^{1}H NMR spectroscopy of P(*n*BA-*co*-AThrOH) (Figure S4), and the molecular weight and dispersity were verified by SEC measurement of the methylated sample (Figure S8).

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.49 (broad, 1H: -COO*H*), 6.82-8.37 (broad, 1H: -N*H*), 3.73-5.25 (broad, 4H: -O-CH_2- in *n*BA, -NH-C*H* and -C*H*-CH_3 in AThrOH), 1.92-2.44 (broad, 1H: -C*H* (main chain) in *n*BA), 1.52 (broad, 2H: -CH_2- in *n*BA), 1.31 (broad, 2H: -CH_2-CH_3 in *n*BA), 1.06 (broad, 3H: -CH-CH_3 in AThrOH), 0.88 (broad, 3H: -CH_2-CH_3 in *n*BA), 0.65-1.88 (broad, C*H* and CH_2 in the main polymer chain) ppm.

The copolymer composition of poly(*n*BA-*co*-AThrOH) was determined by comparison of the ^{1}H NMR peaks corresponding to the two comonomers using the equation (S2)

$$\frac{3x}{3(1-x)} = \frac{Integral\ at\ 0.88\ ppm}{Integral\ at\ 1.06\ ppm} \quad \text{(S2)}$$

where *x* is the fraction of the *n*BA and 1-*x* is the fraction of AThrOH in the random copolymer. The peaks at 0.88 ppm correspond to methyl protons of *n*BA unit (3H), while the peak at 1.06 ppm corresponds to methyl protons of AThrOH (3H).

Synthesis of P(*n*BA-*co*-APheOH)

P(*n*BA-*co*-APheOH) was synthesized using the same copolymerization and purification procedures employed for the synthesis of P(*n*BA-*co*-APhePheOH). The chemical structure and comonomer composition were verified by ^{1}H NMR analysis of P(*n*BA-*co*-APheOH) (Figure S5), and the molecular weight and dispersity were verified by SEC measurement of the methylated sample (Figure S9).

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.64 (broad, 1H: -COO*H*), 7.95 (broad, 1H: -N*H*), 7.18 (broad, 5H: -Ph), 4.43 (broad, 1H: -NH-C*H*), 3.96 (broad, 2H: -O-CH_2- in *n*BA), 2.80-3.09 (broad, 2H: -CH_2-

Ph), 1.51 (broad, 2H: -C*H*$_2$- in *n*BA), 1.30 (broad, 2H: -C*H*$_2$-CH$_3$), 0.87 (broad, 3H: -CH$_2$-C*H*$_3$), 1.07-2.37 (broad, C*H* and C*H*$_2$ in the main polymer chain) ppm.

The copolymer composition of P(*n*BA-*co*-APheOH) was determined by comparison of the ^{1}H NMR peaks corresponding to the two comonomers using the equation (S3)

$$\frac{3x}{1-x} = \frac{Integral\ at\ 0.87\ ppm}{Integral\ at\ 4.43\ ppm} \quad \text{(S3)}$$

where *x* is the fraction of the *n*BA and 1-*x* is the fraction of APheOH in the random copolymer. The peaks at 0.87 ppm correspond to methyl protons of *n*BA unit (3H), while the peak at 4.43 ppm corresponds to tertiary carbon protons of APheOH (1H).

Synthesis of P(*n*BA-*co*-APhePheOH)

For the synthesis of P(*n*BA-*co*-APhePheOH) (Run 10 in Table S1), APhePheOH (549.6 mg, 1.5 mmol), *n*BA (576.8 mg, 4.5 mmol), AIBN (5.00 mg, 0.03 mmol), and dry DMF (3.86 mL) were added in the ampule. The copolymerization was conducted at 60 °C for 24 h. Subsequently, the reaction mixture was poured into a large excess of MeOH/H$_2$O (2/1 volume ratio) and collected by dissolving it in ethanol, and after distilling off the ethanol. The product was finally dried in vacuo at 60 °C overnight to yield P(*n*BA-*co*-APhePheOH) as a semi-transparent solid (yield = 73 %, 0.82 g). The chemical structure and comonomer composition were verified via ^{1}H NMR spectroscopy of P(*n*BA-*co*-APhePheOH) (Figure S6), and the molecular weight and dispersity were verified by SEC measurement of the methylated sample (Figure S10).

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.60 (broad, 1H: -COO*H*), 7.62-9.14 (broad, 2H: -N*H* and -N*H*-CH-COOH), 7.16 (broad, 10H: -Ph), 4.26-4.84 (broad, 2H: -NH-C*H*-CO- and -NH-C*H*-COOH), 3.90 (broad, 2H: -O-C*H*$_2$- in *n*BA), 2.59-3.11 (broad, 4H: -C*H*$_2$-Ph), 1.46 (broad, 2H: -C*H*$_2$- in *n*BA), 1.26

(broad, 2H: -C*H*$_2$-CH$_3$), 0.82 (broad, 3H: -CH$_2$-C*H*$_3$), 1.03-2.35 (broad, C*H* and C*H*$_2$ in the main polymer chain) ppm.

The copolymer composition of P(*n*BA-*co*-APhePheOH) was determined by comparison of the ^{1}H NMR peaks corresponding to the two comonomers using the equation (S4)

$$\frac{3x}{2(1-x)} = \frac{Integral\ at\ 0.82\ ppm}{Integral\ at\ 4.26-4.84\ ppm} \quad \text{(S4)}$$

where *x* is the fraction of the *n*BA and 1-*x* is the fraction of APhePheOH in the random copolymer. The peaks at 0.82 ppm correspond to methyl protons of *n*BA unit (3H), while the peak at 4.26-4.84 ppm corresponds to tertiary carbon protons of APhePheOH (2H).

RAFT synthesis of P(*n*BA-*co*-AGluOH)

For the synthesis of a representative P(*n*BA-*co*-AGluOH) by RAFT copolymerization (Run 12 in Table S3), AGluOH (301.8 mg, 1.5 mmol), *n*BA (576.8 mg, 4.5 mmol), AIBN (5.00 mg, 0.03 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (21.9 mg, 0.06 mmol) and dry EtOH (2.87 mL) were added in the ampule. After degassing the mixture, the copolymerization was conducted at 60 °C for 24 h, followed by the purification as described for the synthesis of P(*n*BA-*co*-AGluOH) by free radical copolymerization. RAFT-synthesized P(*n*BA-*co*-AGluOH) was finally obtained as a yellow solid (yield = 93%, 814.5 mg).

Instrumentation.

The proton nuclear magnetic resonance (^{1}H NMR, 400 MHz) was recorded on a JEOL JNM-ECX400 using deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform ($CDCl_3$) as a solvent and

tetramethylsilane (TMS) as an internal standard. The number-average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution (M_w/M_n) were estimated by SEC using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column setup comprised four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limited molecular weight): α-M (13 μm, $>1 \times 10^7$), α-4000 (10 μm, 4×10^5), α-3000 (7 μm, 9×10^4), α-2500 (7 μm, 5×10^3), 30 cm each] and a guard column [TSK-guardcolumn α, 4.0 cm]. The system was operated at the flow rate 1.0 mL/min using DMF containing 10 mM LiBr as the eluent. Polystyrene standards (Tosoh) in the range 1050–1,090,000 were employed for calibration. Thermogravimetric analysis (TGA) was carried out on a SEIKO TGA/6200 at a heating rate of 10 °C/min under nitrogen atmosphere, and DSC analysis was performed using a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C/min under nitrogen. Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were recorded on a Jasco FT-IR460Plus spectrometer using the ATR accessory with a ZnSe crystal. The film sample was prepared by a hot-press. The circular dichroism (CD) was measured using a JASCO J-720 spectropolarimeter. The solid sample for CD measurement was prepared by drop-casting of hexafluoroisopropanol (HFIP) solution on a quartz plate, followed by drying at 100 °C on a hot plate.

Tensile tests were performed using a MX2-500N (IMADA Co., Ltd.) with a digital force gauge ZTA-500N machine (IMADA Co., Ltd.). The dog bone-shaped specimen (effective gauge dimensions: length = 12 mm, width = 2 mm, and thickness = <1.0 mm) was prepared using a Teflon mold at 100−120 °C by a hot-press for 1−3 min, at where the temperature was adjusted to achieve molten states, followed by cooling at an ambient condition (Table S4). Each test was repeated at least three times. The Young's modulus (E) was determined by the initial slope (low strain area < 5%).

To quantitatively evaluate the self-healing efficacy of the amino acid-bearing acrylamides/*n*-butyl acrylate copolymers, the dog bone-shaped specimens prepared by the hot-press were cut into two species and then compressed using a laboratory clamp to allow healing at 40 °C on a hot plate for different duration of time. The stress-strain curves of the healed samples were collected by same procedure as the pristine samples. The mechanical healing efficacy was calculated as follows:[12,13]

$$Healing\ efficacy\ =\ \frac{Max.\ strength\ Healed}{Max.\ strength\ Pristine} \times 100\%$$

The transparency was evaluated measured by UV-vis measurement using a JASCO V-630BIO UV−vis spectrophotometer. The samples were prepared by drop-casting as follows: 5 mg of the copolymer DMF solution (1.0 wt %) was placed on the glass substrate, and it was allowed to evaporate overnight in an ambient atmosphere. Wavelength-dependent refractive indices $n(\lambda)$ of spin-coated polymer thin films were evaluated by a spectroscopic ellipsometer (J.A. Woollam M-2000U), as described previously.[14,15] Briefly, Cauchy function for the refractive index $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$ was employed for evaluation of the wavelength-dependence of refractive index. The accuracy of the refractive index was confirmed by Coefficients of Cauchy's relation determined by least squares fit for more than four different refractive indexes. The homogenous polymer thin films were prepared by spin-coating from DMF solutions (conc. = 3.0 wt %, 1000 rpm at 90 s) on a silicon wafer. The Abbe number (ν_D) was calculated for the polymers as $\nu_D = (n_D–1)/(n_F–n_C)$, where n_D, n_F, and n_C are the refractive indices of materials at wavelength of 589.3, 486.1, and 656.3 nm, that correspond to sodium D, hydrogen F, and hydrogen C line, respectively.

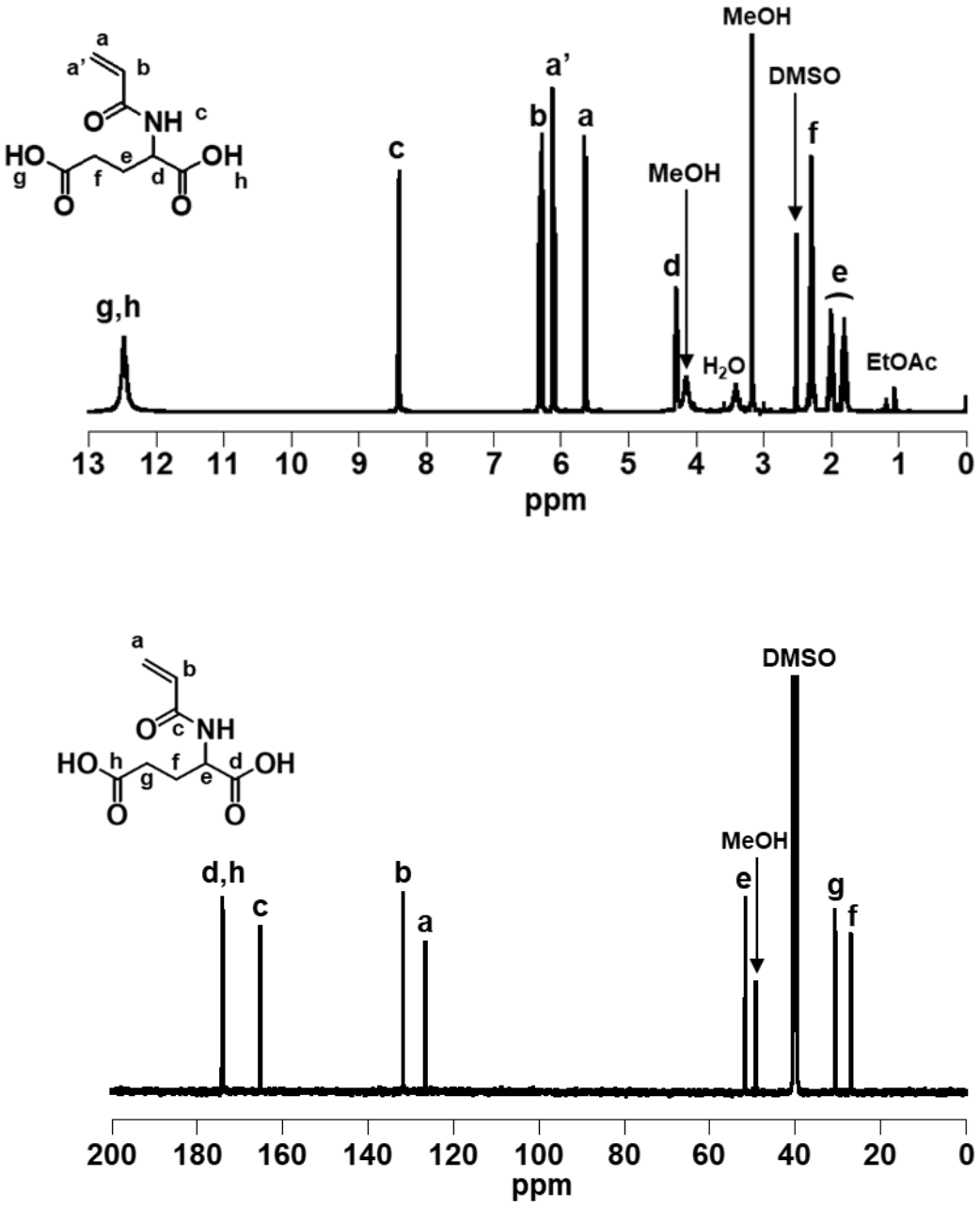


Figure S1. ^{1}H and ^{13}C NMR spectra of *N*-acryloyl-L-glutamic acid (AGluOH) in DMSO-d_6.

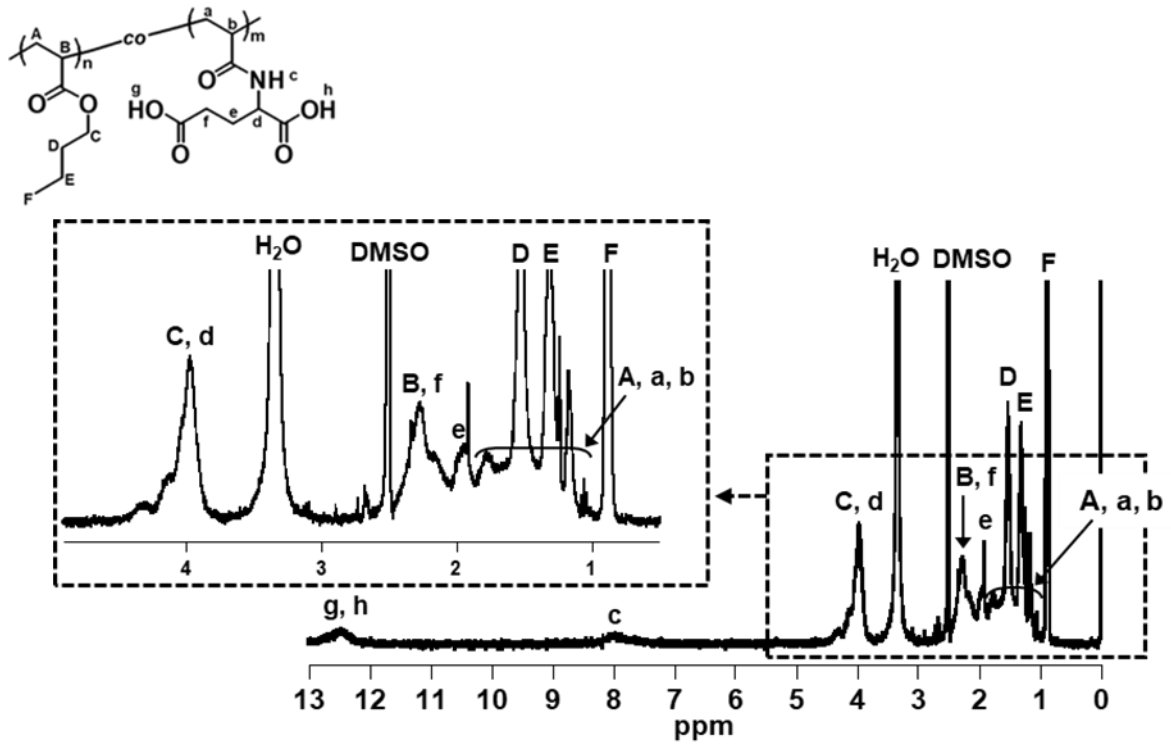


Figure S2. ^{1}H NMR spectrum of P(*n*BA-*co*-AGluOH) in DMSO-d_6 (Run 6 in Table S1).

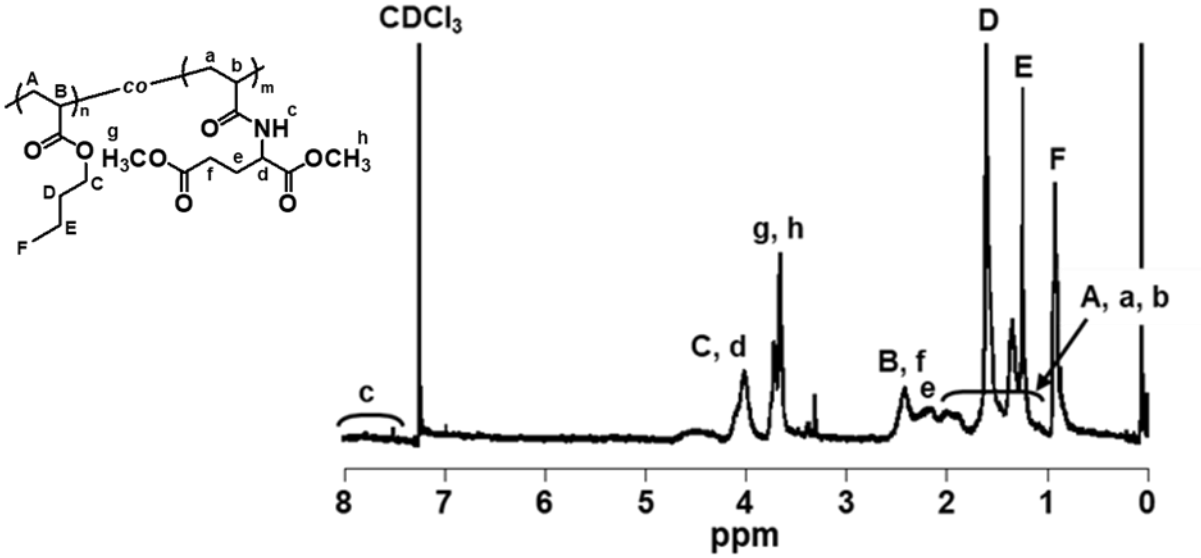


Figure S3. ^{1}H NMR spectrum of methylated copolymer, P(*n*BA-*co*-AGluOMe), in $CDCl_3$ (Run 6 in Table S1).

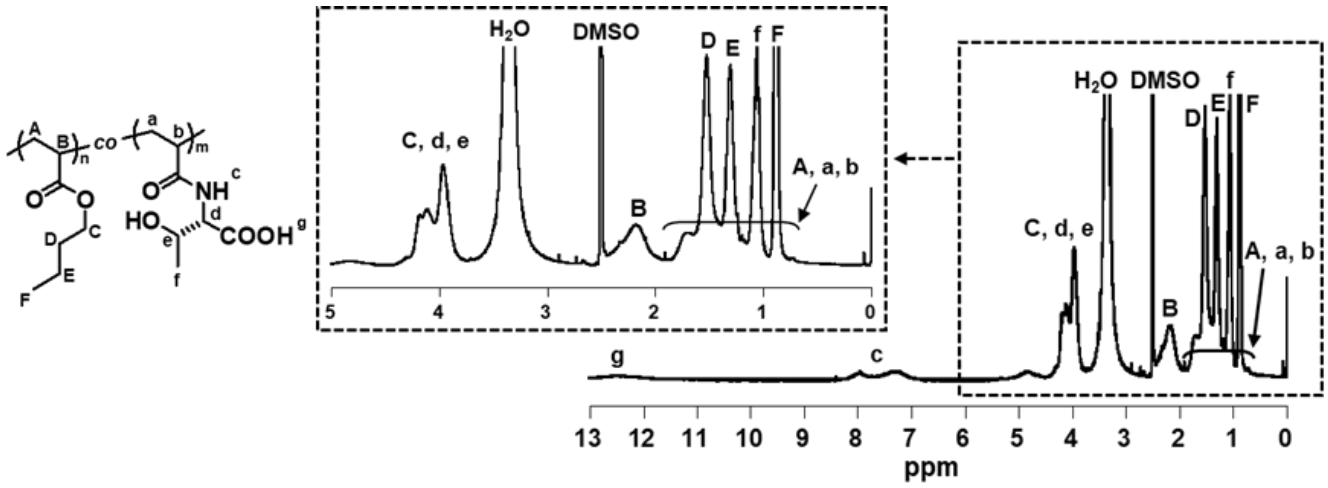


Figure S4. [1]H NMR spectrum of P(*n*BA-*co*-AThrOH) in DMSO-d_6 (Run 2 in Table S1).

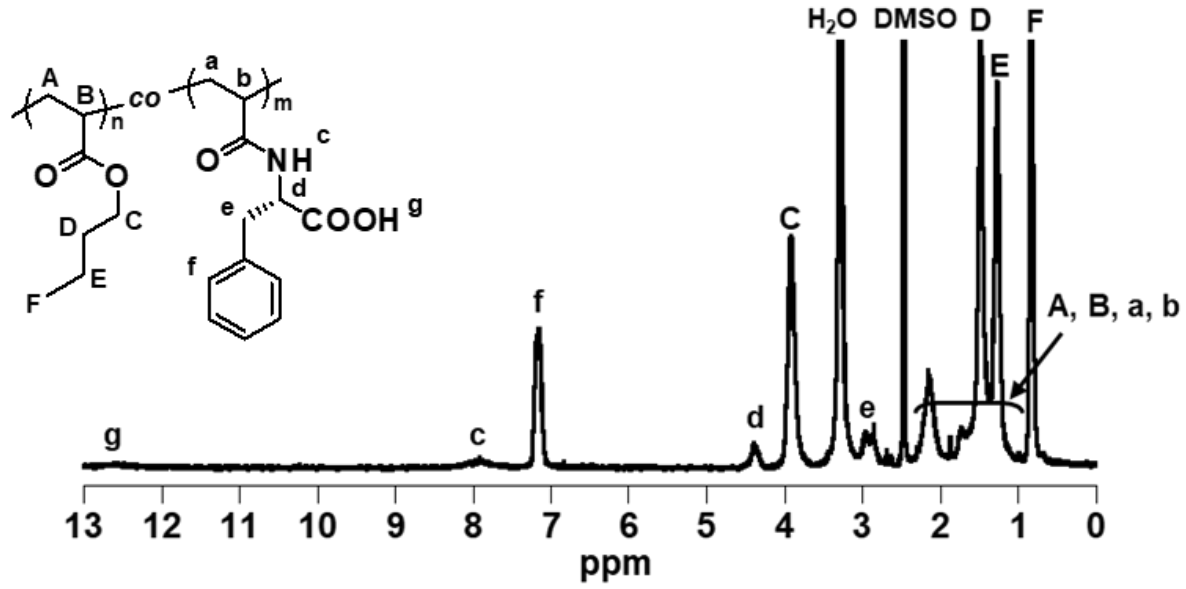


Figure S5. [1]H NMR spectrum of P(*n*BA-*co*-APheOH) in DMSO-d_6 (Run 9 in Table S1).

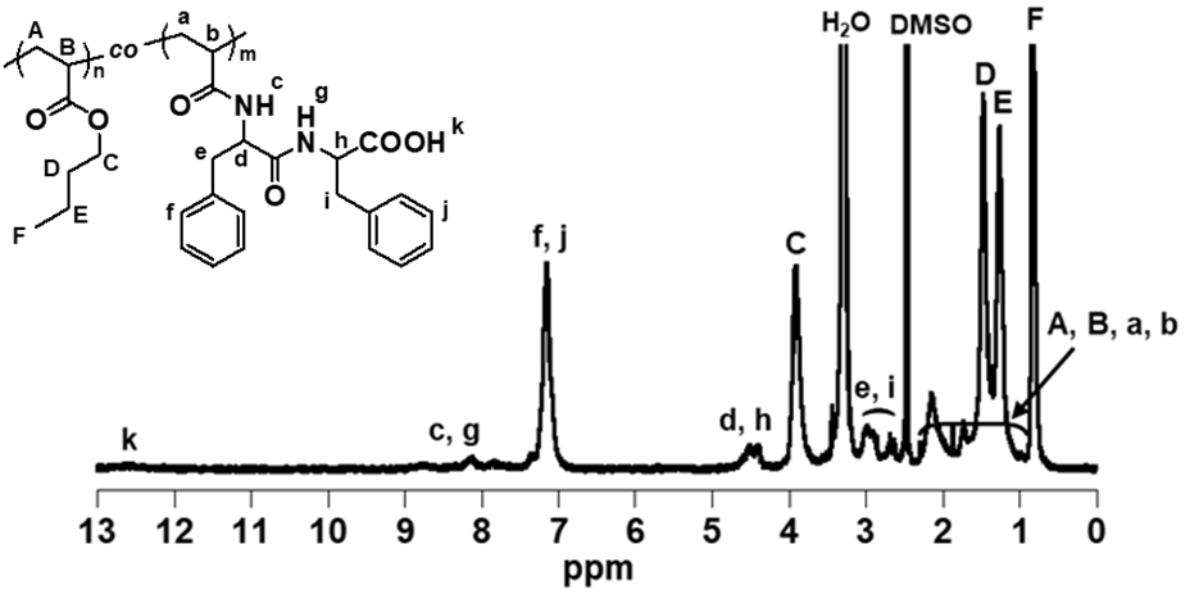


Figure S6. ^{1}H NMR spectrum of P(*n*BA-*co*-APhePheOH) in DMSO-d_6 (Run 10 in Table S1).

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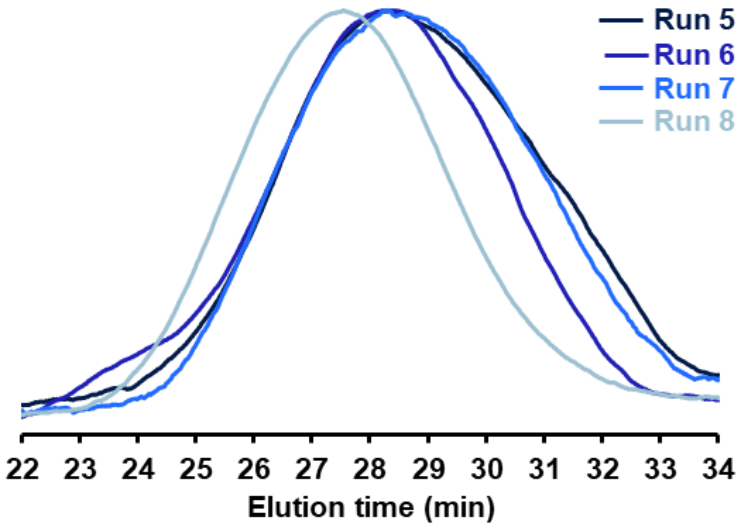


Figure S7. SEC traces of P(*n*BA-*co*-AGluOMe)s.

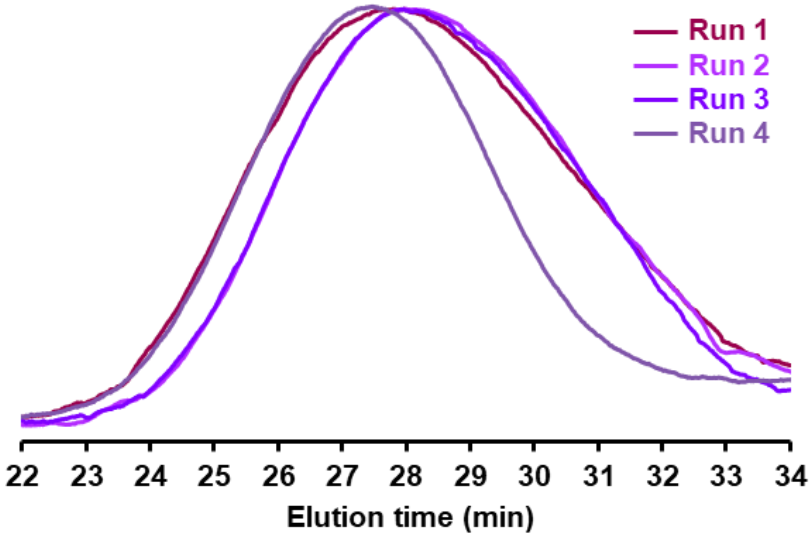


Figure S8. SEC traces of P(*n*BA-*co*-AThrOMe)s.

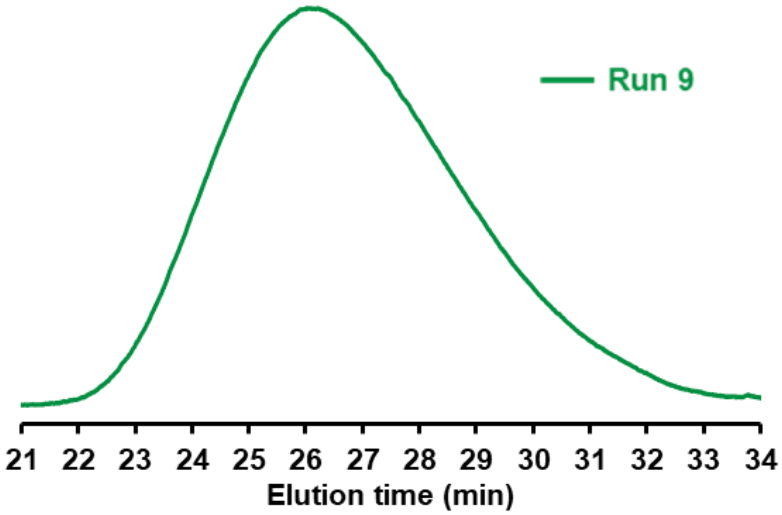


Figure S9. SEC trace of P(*n*BA-*co*-APheOMe).

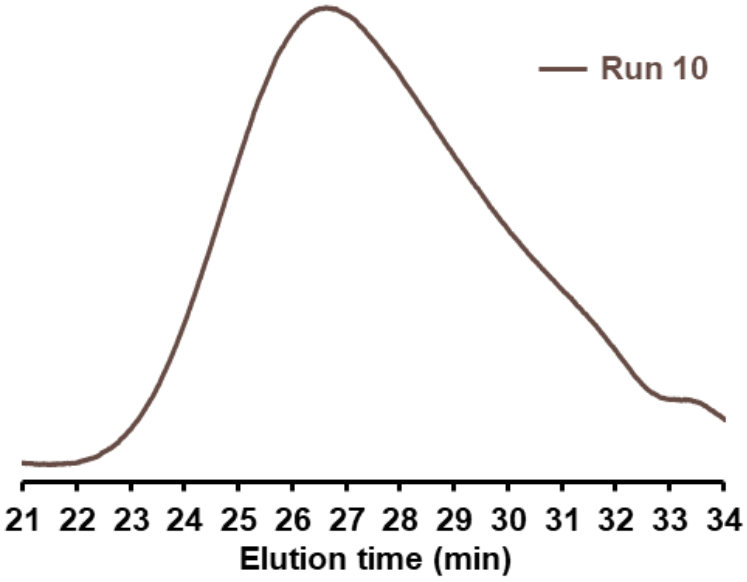


Figure S10. SEC trace of P(*n*BA-*co*-APhePheOMe).

Table S1. Characteristics of random copolymers prepared by free radical copolymerization[a)]

Run	Copolymer	[I]/[*n*BA]/[Amino acid-based monomer]	Yield	M_n[f)] (SEC)	M_w[f)] (SEC)	M_w/M_n[f)]	n:m	T_{d5}[i)] (°C)	T_g[j)] (°C)
1[b)]	P(*n*BA-*co*-AThrOH)	1/50/150	90[d)]	21700	68800	3.17	35:65[g)]	187	134.1
2[b)]		1/100/100	88[d)]	19900	54800	2.75	58:42[g)]	195	94.5
3[b)]		1/150/50	88[d)]	18400	55700	3.03	80:20[g)]	200	27.3
4[b)]		1/175/25	81[d)]	30800	60000	2.57	90:10[g)]	213	-37.8
5[b)]	P(*n*BA-*co*-AGluOH)	1/50/150	98[d)]	16400	42600	2.60	51:49[h)]	254	55.1
6[b)]		1/100/100	88[d)]	15100	36700	2.42	68:32[h)]	255	47.7
7[b)]		1/150/50	95[d)]	18300	47300	2.58	82:18[h)]	270	16.5
8[b)]		1/175/25	74[d)]	29400	60400	2.06	92:8[h)]	280	-20.5
9[c)]	P(*n*BA-*co*-APheOH)	1/150/50	68[e)]	46400	116500	2.51	88:12[g)]	309	-5.1
10[c)]	P(*n*BA-*co*-APhePheOH)	1/150/50	73[e)]	27200	76900	2.83	86:14[g)]	288	21.5

[a)] Copolymerization was conducted with AIBN at 60 °C for 24 h in [b)] ethanol and [c)] DMF (monomer concentration. = 0.25 g/mL). [d)] *n*-Hexane insoluble part. [e)] MeOH/H_2O (2/1 volume ratio) insoluble part. [f)] Methylated samples were analyzed by size-exclusion chromatography (SEC) utilizing polystyrene standards in *N*,*N*-dimethylformamide (DMF; 10 mM LiBr). [g)] Calculated utilizing ^{1}H NMR spectroscopy in DMSO-d_6. [h)] Calculated utilizing ^{1}H NMR spectra of the methylated samples in $CDCl_3$. [i)] 5 wt% loss temperature. [j)] Glass transition temperature.

Table S2. Solubilities of threonine-containing copolymers, homopolymer, and monomer

Solvent	P(*n*BA)	AThrOH	P(AThrOH)	P(*n*BA-*co*-AThrOH) n:m = 35:65	P(*n*BA-*co*-AThrOH) n:m = 58:42	P(*n*BA-*co*-AThrOH) n:m = 79:21
MeOH	-	+	+	+	+	+
EtOH	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
Acetone	+	-	-	-	+	+
DCM	+	-	-	-	-	+
$CHCl_3$	+	-	-	-	-	+
THF	+	+	-	-	+	+
EtOAc	+	+	-	-	-	+
Et_2O	+	-	-	-	-	-
Dioxane	+	+	-	-	+	+
Hexane	+	-	-	-	-	-
H_2O (pH = 1)	-	+	+	-	-	-
H_2O (pH = 7)	-	+	+	+	-	-
H_2O (pH = 12)	-	+	+	+	+	-

+ : Soluble at room temperature. - : Insoluble at room temperature.

Table S3. Solubilities of glutamic acid-containing copolymers, homopolymer, and monomer

Solvent	AGluOH	P(AGluOH)	P(*n*BA-*co*-AGluOH) 51:49	P(*n*BA-*co*-AGluOH) 68:32	P(*n*BA-*co*-AGluOH) 82:18
MeOH	+	+	+	+	+
EtOH	+	+	+	+	+
DMSO	+	+	+	+	+
DMF	+	+	+	+	+
Acetone	-	-	-	-	-
DCM	-	-	-	-	-
$CHCl_3$	-	-	-	-	-
THF	+	-	-	+	+
EtOAc	+	-	-	-	-
Et_2O	-	-	-	-	-
Dioxane	+	-	-	-	+
Hexane	-	-	-	-	-
H_2O (pH = 1)	+	+	-	-	-
H_2O (pH = 7)	+	+	-	-	-
H_2O (pH = 12)	+	+	+	+	+

+ : Soluble at room temperature. - : Insoluble at room temperature.

Table S4. Solubilities of phenylalanine- and diphenylalanine-containing copolymers

Solvent	P(*n*BA-*co*-APheOH) 68:32	P(*n*BA-*co*-APhePheOH) 82:18
MeOH	+	+
EtOH	+	-
DMSO	+	+
DMF	+	+
Et_2O	-	-
Hexane	-	-
H_2O (pH = 7)	-	-

+ : Soluble at room temperature. - : Insoluble at room temperature.

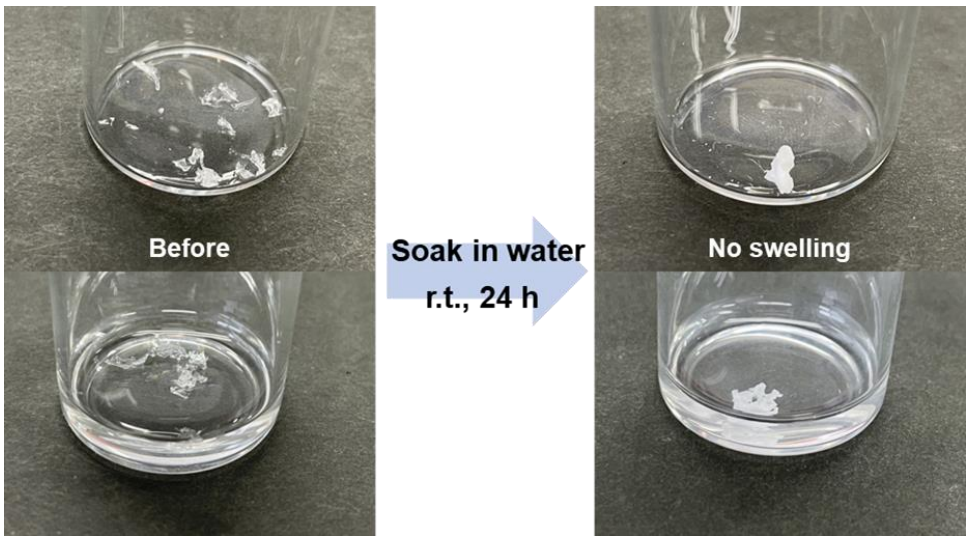


Figure S11. Photos of P(*n*BA-*co*-AGluOH) with 82 mol% *n*BA content in neutral water (1.0 wt%)

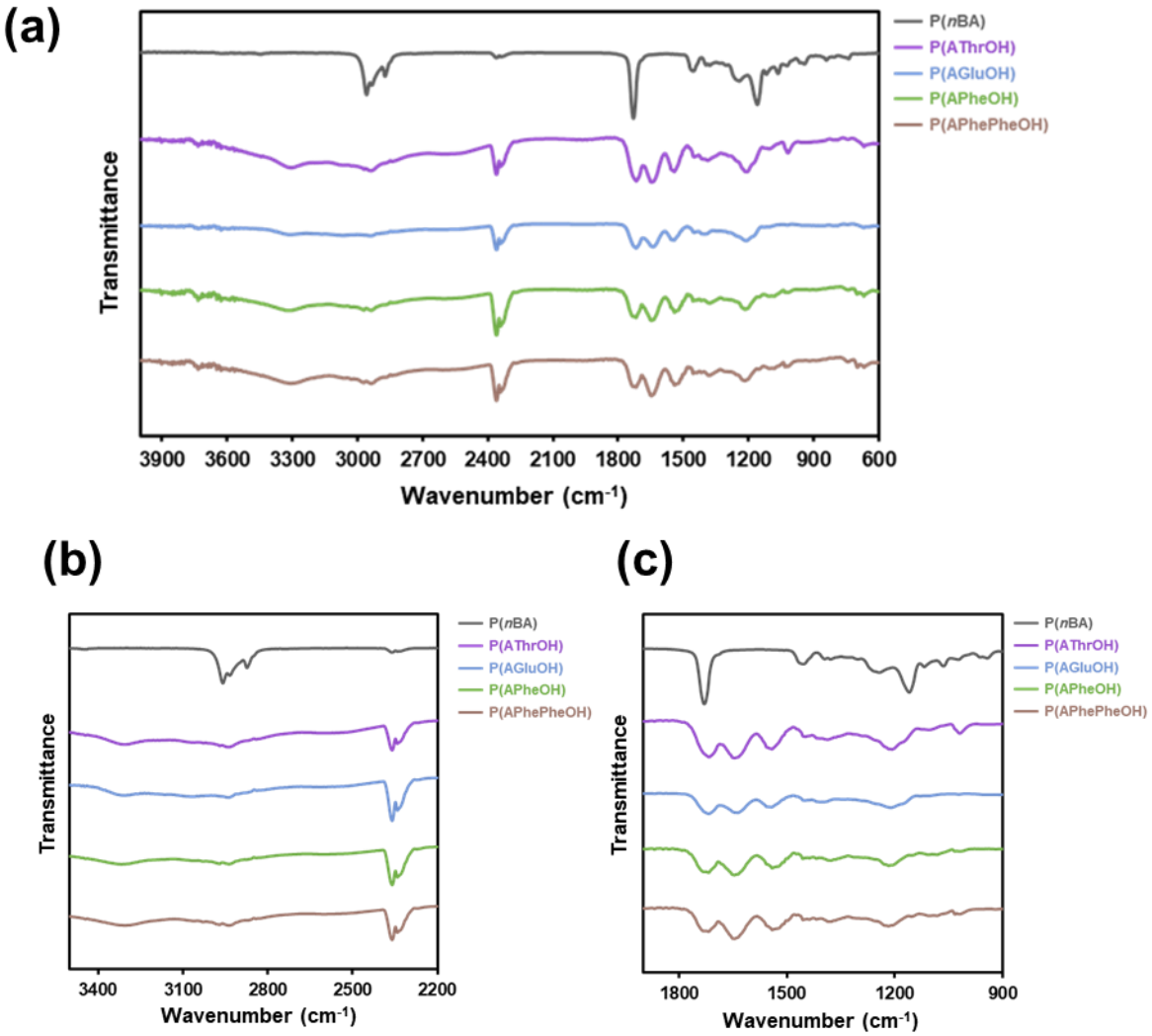


Figure S12. (a) ATR FT-IR spectra of amino acid-based homopolymers and P*n*BA, and magnification in the region of (b) N-H band and (c) carbonyl band.

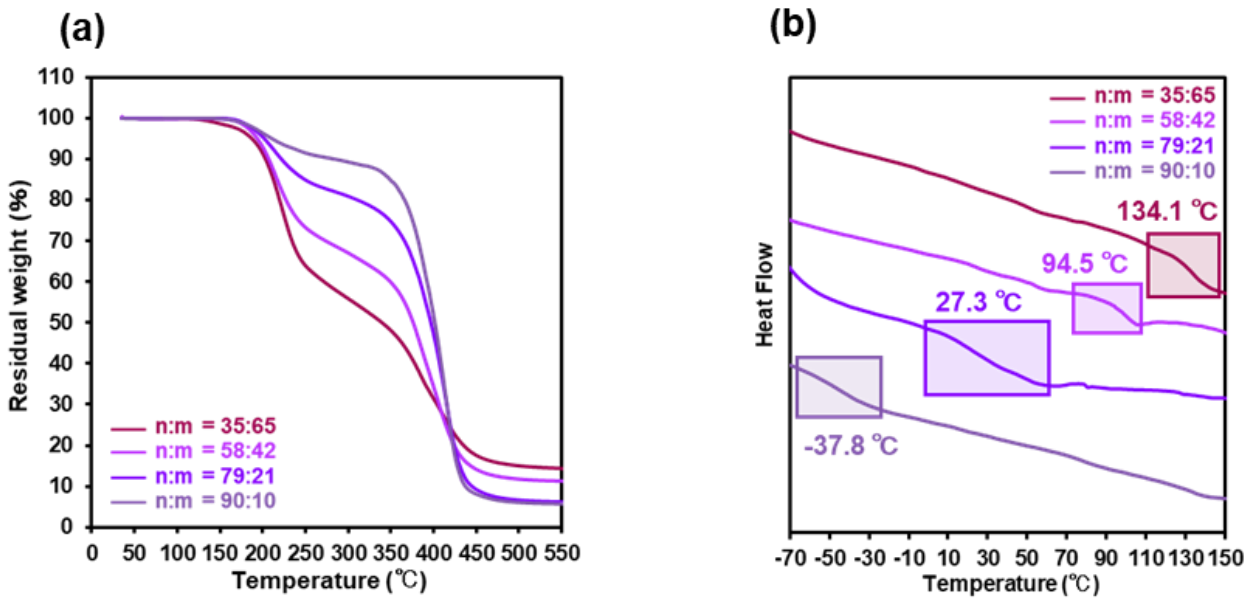


Figure S13. (a) TGA traces (b) DSC traces of P(*n*BA-*co*-AThrOH)s (Run 1-4 in Table S1).

Table S5. Thermal properties of P(*n*BA-*co*-AThrOH)s.

n:m	T_{d5} [a] (℃)	T_{d10} [b] (℃)	Residual weight [c] (%)	T_g [d] (℃)
35:65	187	203	14.0	134.1
58:42	195	208	11.2	94.5
79:21	200	220	6.1	27.3
90:10	213	286	5.7	-37.8

[a] The 5 wt-% loss temperature. [b] The 10 wt-% loss temperature. [c] Residual weight of the sample heated at 10 ℃/min until 550 ℃ in TGA under nitrogen. [d] Glass transition temperature.

Table S6. Sample preparation conditions for tensile test

Run	Copolymer	n:m	Hot press
1	P(*n*BA-*co*-AThrOH)	35:65	120 ℃, 3 min
2		58:42	120 ℃, 3 min
3		80:20	100 ℃, 1 min
4		90:10	-
5	P(*n*BA-*co*-AGluOH)	51:49	-
6		68:32	120 ℃, 3 min
7		82:18	100 ℃, 1 min
8		92:8	-
9	P(*n*BA-*co*-APheOH)	88:12	100 ℃, 1 min
10	P(*n*BA-*co*-APhePheOH)	86:14	100 ℃, 1 min
11	P(*n*BA-*co*-AGluOH)	82:18	100 ℃, 1 min
12			
13			
14		81:19	

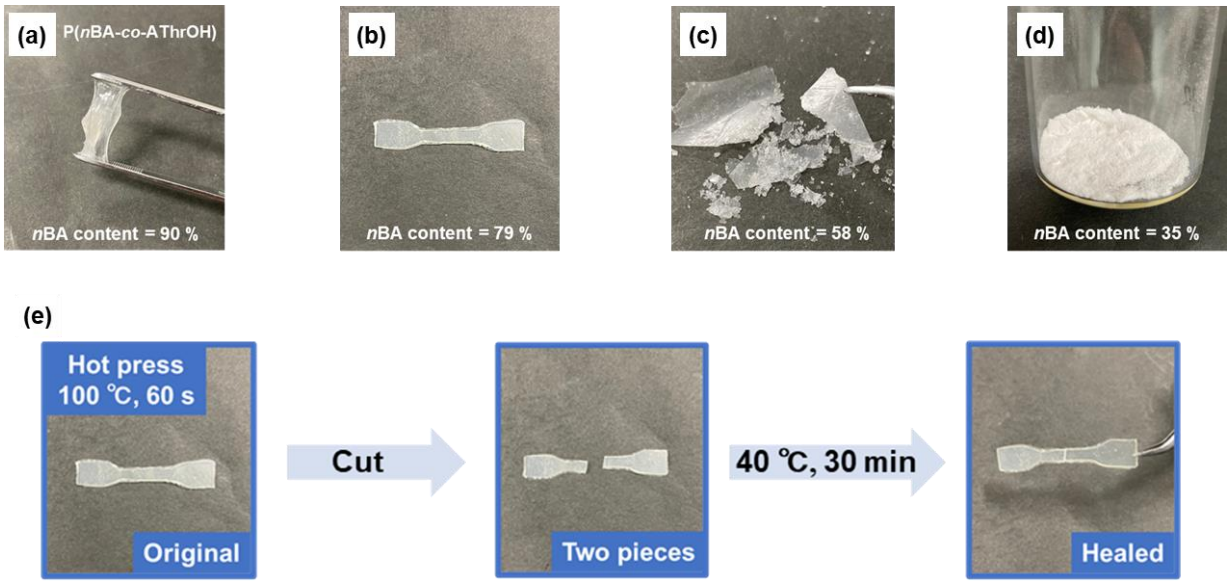


Figure S14. (a-d) Appearance of P(*n*BA-*co*-AThrOH)s (*n*BA content = 35-90 mol-%), (e) Photos of preliminary healing test of P(*n*BA-*co*-AThrOH) (*n*BA content = 80 mol-%).

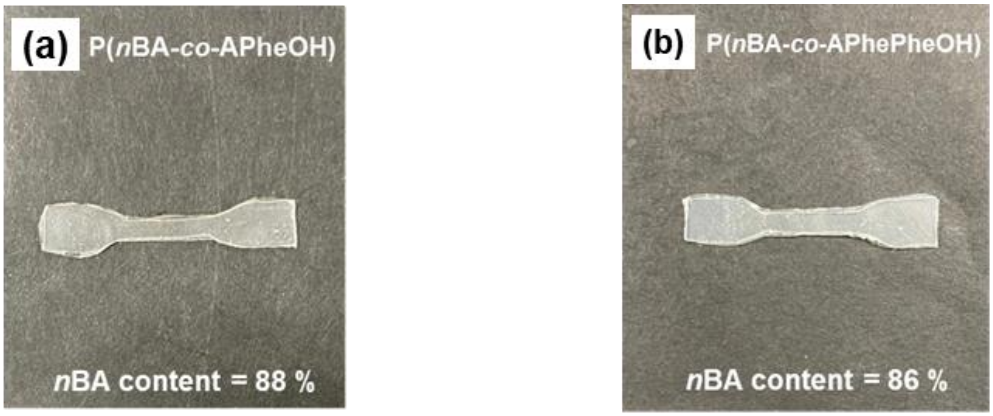


Figure S15. Appearance of (a) P(*n*BA-*co*-APheOH) and (b) P(*n*BA-*co*-APhePheOH).

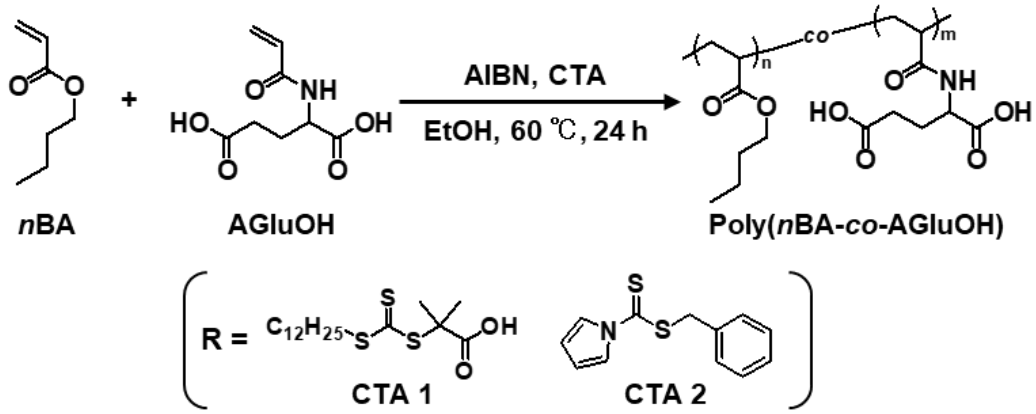
Table S7. Preliminary healing test of amino acid-based copolymers.

Run	Copolymer	Self-healing
3	P(*n*BA-*co*-AThrOH)	40 ℃, 30 min
7	P(*n*BA-*co*-AGluOH)	25 ℃, 30 s
9	P(*n*BA-*co*-APheOH)	no healing
10	P(*n*BA-*co*-APhePheOH)	

Table S8. Mechanical parameters of P(*n*BA-*co*-AGluOH) and P(*n*BA-*co*-AThrOH) after healing.

Sample		Young's modulus [a)] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness [b)] (MJ/m^3)	Self-healing efficacy [c)] (%)
P(*n*BA-*co*-AGluOH) (Run 7)	Original	97	5.2	385	17.30	-
	40 ℃, 1 min	93	1.4	4.71	0.49	3.0
	40 ℃, 5 min	67	3.7	36.1	1.20	7.0
	40 ℃, 10 min	97	2.8	269	6.70	39
	40 ℃, 30 min	71	4.1	466	15.5	90
P(*n*BA-*co*-AThrOH) (Run 3)	Original	148	11.0	8.8	0.54	-
	40 ℃, 30 min	111	2.6	2.2	0.028	5.0
	40 ℃, 1 h	191	3.3	2.6	0.052	9.6
	40 ℃, 3 h	147	3.9	2.9	0.062	11.0

[a)] Calculated from stress at small strain (<5%). [b)] Estimated by area under stress–strain until fracture point. [c)] Based on toughness.



Scheme S2. Synthesis of P(*n*BA-*co*-AGluOH)s by RAFT polymerization.

Table S9. Characteristics of P(*n*BA-*co*-AGluOH)s(*n*BA content = approximately 80 mol%).

Run	[I]/[CTA]/[*n*BA]/[AGluOH]	M_n[c] (SEC)	M_w[c] (SEC)	M_w/M_n[c]	n:m[d]	T_{d5}[e] (℃)	T_g[f] (℃)	Young's modulus[g] (MPa)	Maximum strength (MPa)	Maximum strain (%)	Modulus of toughness[h] (MJ/m^3)
7	1/0/150/50	18300	47300	2.58	82:18	270	16.5	97	5.2	385	17.30
11	1/0/300/100	21500	54000	2.73	82:18	272	-17.5	90	4.8	634	22.28
12[a]	1/2/150/50	9500	11900	1.25	82:18	268	0.8	5.0	0.39	298	0.59
13[a]	1/2/300/100	14700	20000	1.36	82:18	270	-4.2	92	2.42	396	0.78
14[a]	1//2/600/200	15900	28500	1.79	81:19	273	-6.0	66	1.94	710	12.03

[a] Synthesis by CTA 1. [c]Methylated samples were analyzed by size-exclusion chromatography (SEC) utilizing polystyrene standards in *N*,*N*-dimethylformamide (DMF; 10 mM LiBr). [d] Calculated by ^{1}H NMR spectroscopy of methylated samples in $CDCl_3$. [e] 5 wt% loss temperature. [f] Glass transition temperature. [g] Calculated from stress at small strain (<5%). [h] Estimated by area under the stress–strain until the fracture point.

Table S10. Synthesis of P(*n*BA-*co*-AGluOH)s by RAFT polymerization[a)]

Run	[I]/[CTA]/[*n*BA]/[AGluOH]	Yield (%)	M_n [d)] (theory)	M_n [e)] (SEC)	M_w [e)] (SEC)	M_w/M_n [e)]	n:m [f)]
15	1/2/75/25	>99 [b)]	7500	7800	10100	1.30	82:18
16	1/2/50/150	60 [c)]	11200	10100	13700	1.36	39:61
17	1/2/100/100	85 [c)]	14200	12500	17700	1.42	68:32
18	1/2/150/50	83 [c)]	12400	11200	15600	1.40	83:17

[a)] Synthesis by CTA 2. Monomer conc. = 0.25 g/mL. [b)] *n*-Hexane insoluble part. [c)] Dialysis in MeOH for 3 days. [d)] The theorical molecular weight ($M_{n,theory}$) = ($M_{monomer}$) × ($[M1]_0 + [M2]_0$)/[CTA] × yield + (MW of CTA) : $M_{monomer} = A_1F_1 + A_2F_2$ (A = molecular weight, F = molar fraction). [e)] Methylated samples were measured by size-exclusion chromatography (SEC) using polystyrene standards in *N*,*N*-dimethylformamide (DMF, 10 mM LiBr). [f)] Calculated by ^{1}H NMR in of poly(*n*BA-*co*-AGluOMe) in $CDCl_3$.

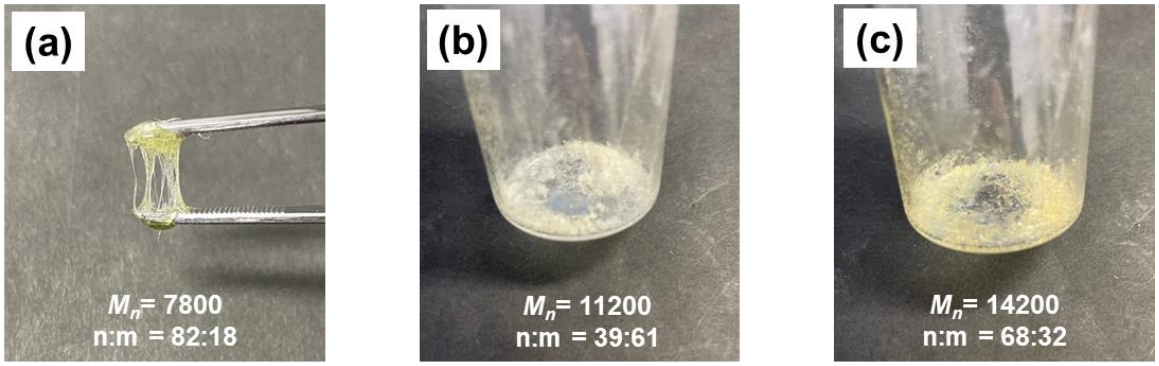


Figure S16. (a-c) Appearance of P(*n*BA-*co*-AGluOH)s prepared by RAFT polymerization with a dithiocarbamate-type CTA (CTA2).

Table S11. Optical properties of P(*n*BA-*co*-AGluOH)s (*n*BA content = 51–82 mol-%).

n:m	Film thickness (nm)	n_D (589 nm)	n_F (486 nm)	n_d (587 nm)	n_c (656 nm)	v_D
51:49	95.4	1.5089	1.5155	1.5090	1.5065	56.7
68:32	94.1	1.5021	1.5084	1.5022	1.4999	58.6
82:18	85.1	1.4883	1.4939	1.4883	1.4862	63.5

[a)] Film thickness, refractive index, and Abbe number of the copolymers were determined by ellipsometry. Polymer thin films were prepared by spin coating.

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