Electronic supplementary information (ESI)

RAFT-Synthesis and Self-Assembly-Induced Emission of Pendant Diphenylalanine–Tetraphenylethylene Copolymers

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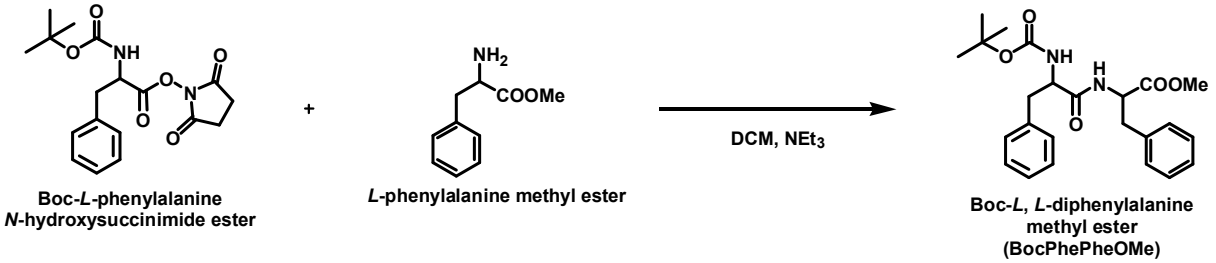
Experimental Section

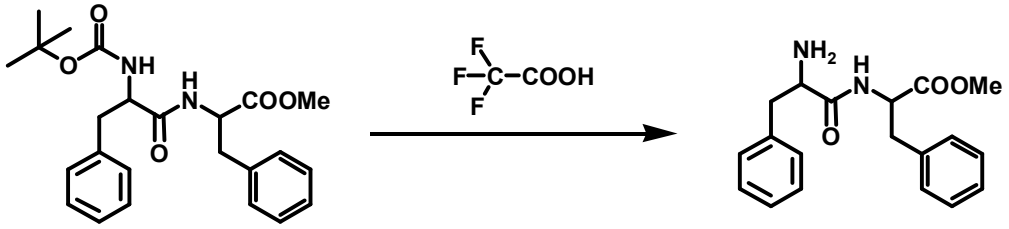
Materials. 2,2'-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97 %) was purified by recrystallization from methanol. *N*,*N*-Dimethylformamide (dehydrated DMF, Kanto Chemical, 99.5%), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (Aldrich, 98%), thioflavin T (ThT, Wako) were used as received. *N*-Acryloyl-*L*,*L*-diphenylalanine (APhePheOH),[1] *N*-acryloyl-*L*,*L*-diphenylalanine methyl ester (APhePheOMe)[2, 3] and 4-(1,2,2 triphenylvinyl) phenyl acrylate (ATPE)[4] were synthesized as reported previously. The methylation agent, trimethylsilyldiazomethane (10% in hexane, TCI), was purchased and used as received. P(APhePheOH),[1] P(APghePheOMe),[2, 3] and P(ATPE)[4] homopolymers were prepared as reported previously.

Synthesis of Boc-*L,L*-diphenylalanine methyl ester (BocPhePheOMe)[5]



BocPhePheOMe was prepared according to a reported procedure[1] with some modifications. A solution of Boc-L-phenylalanine *N*-hydroxysuccinimide ester (2.41 g, 6.65 mmol), L-phenylalanine methyl ester(1.43 g, 6.65 mmol), and triethylamine (1.85 mL, 13.0 mmol) were dissolved in dichloromethane (75 mL). After the solution was stirred at room temperature for 24 h, the mixture was washed with 1M HCl (2 x 50mL), sodium bicarbonate (2 x 50 mL), and brine (1 x 50 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure. The crude product was purified on a silica gel using solid column chromatography with ethyl acetate/dichloromethane (1:4 vol/vol) as eluting solvent to give BocPhePheOMe as white solid (2.20 g, 77%). ^{1}H NMR (400MHz, DMSO-d_6): δ 8.31 (dd, 1H: -N*H*), 7.26-7.12 (m, 10H: -phenyl), 6.86 (dd, 1H: -N*H*), 4.46 (m, 1H: -NHC*H*CH_2-phenyl), 4.16 (t, 1H: -NHC*H*$COOCH_3$), 3.54 (s, 3H: -COO-CH_3), 2.97-2.65 (m, 4H: -CH_2-phenyl), 1.25 (s, 9H: -C(CH_3)$_3$) ppm.

Deprotection of Boc-protected dipeptide (BocPhePheOMe)[3, 6]

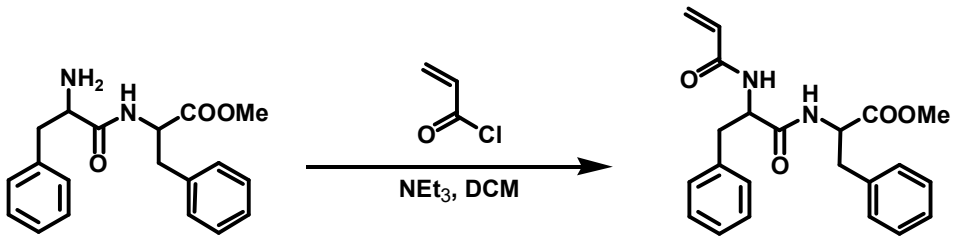


Boc-*L*,*L*-diphenylalanine methyl ester (BocPhePheOMe)

NH_2-*L*,*L*-diphenylalanine methyl ester (NH_2PhePheOMe)

The Boc-protected dipeptide (2.20 g, 5.15 mmol) was dissolved in trifluoroacetic acid (TFA, 5.90 mL) and dichloromethane (10.0 mL), and the reaction mixture was stirred at room temperature for 45 min. After removal of TFA under reduced pressure, it was reprecipitated into diethyl ether to obtain *L,L*-diphenylalanine methyl ester (NH_2PhePheOMe) as a white solid (1.60 g, 95%). ^{1}H NMR (400MHz, DMSO-d_6): δ 8.91 (d, 1H: -N*H*), 7.96 (s, 2H: -NH_2), 7.32-7.18 (m, 10H: -phenyl), 4.52 (m, 1H: -NHC*H*CH_2-phenyl), 4.03 (m, 1H: -NHC*H*$COOCH_3$), 3.54 (s, -COO-CH_3), 3.11-2.90 (m, 4H: -CH_2-phenyl) ppm.

Synthesis of *N*-acryloyl-*L*,*L*-diphenylalanine methyl ester (APhePheOMe)[2, 3]



NH_2PhePheOMe APhePheOMe

NH_2PhePheOMe (1.50 g, 4.60 mmol) was dissolved in dry dichloromethane (50 ml). After adding 2.0 equiv. of triethylamine (1.28 ml, 9.2 mmol) to the solution, 1.1 equiv. of acryloyl chloride (0.41 ml, 5.06 mmol) was added dropwise at 0°C. The mixture was then stirred at room temperature for overnight. The reaction mixture was washed with 1M HCl (2 x 50mL), sodium bicarbonate (2 x 50 mL), and brine (1 x 50 mL). The organic layer was dried with magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The product was recrystallized from dichloromethane. The product was finally dried under vacuum at room temperature to afford a white solid (1.05 g, 60%).

^{1}H NMR (400MHz, DMSO-d_6): δ 8.56 (dd, 1H: -N*H*), 8.28 (dd, 1H: -N*H*), 7.24-7.11 (m, 10H: -phenyl), 6.22 (q, 1H: -C*H*=CH_2), 5.98-5.49 (d, 2H: -CH=CH_2), 4.61 (t, 1H: -NHC*H*CH_2-phenyl), 4.45 (t, 1H: -NHC*H*$COOCH_3$), 3.54 (s, 3H: -COO-CH_3), 3.02-2.82 (m, 2H, -CH_2-phenyl), 2.72-2.63 (m, 2H, -CH_2-phenyl) ppm.

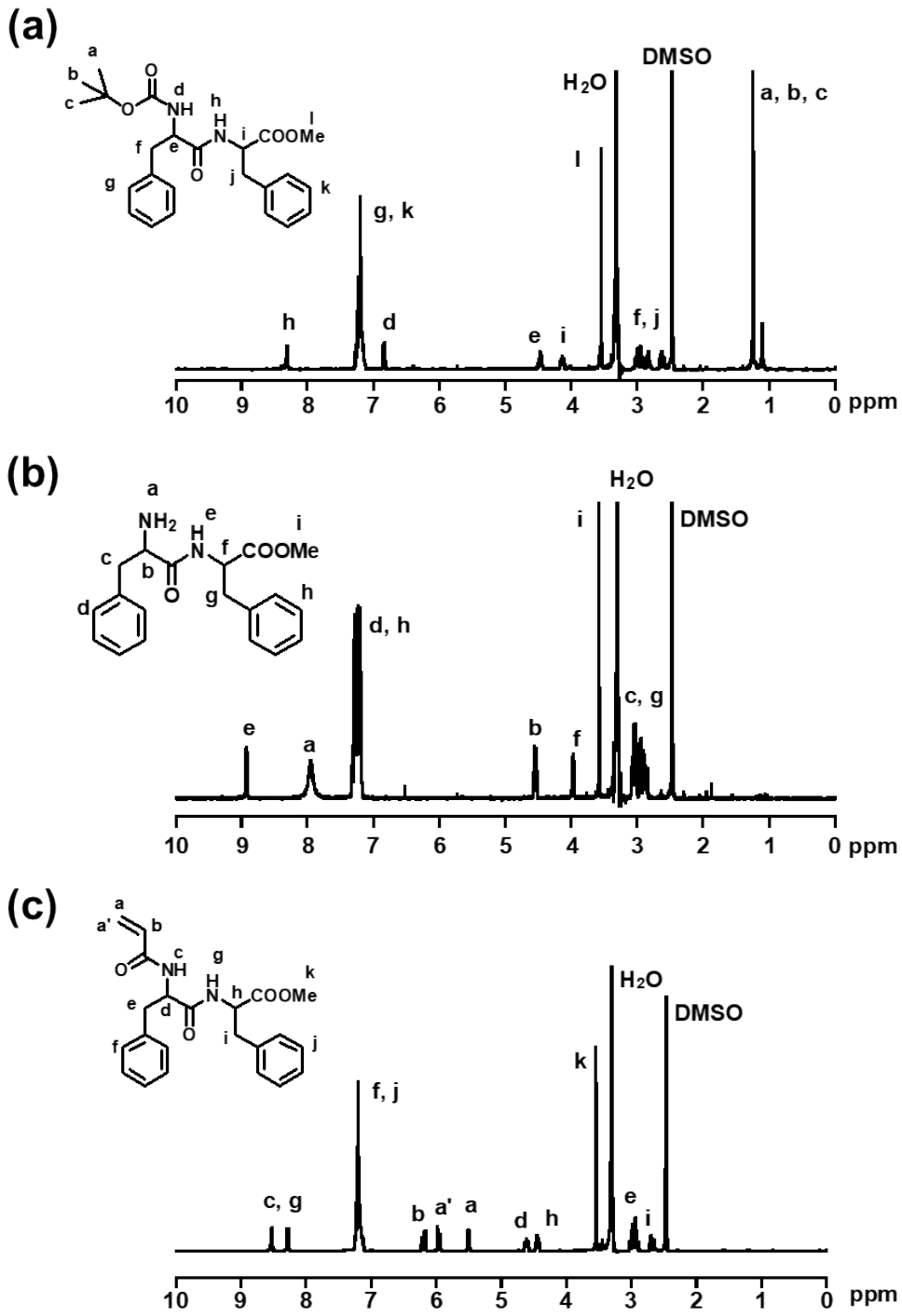
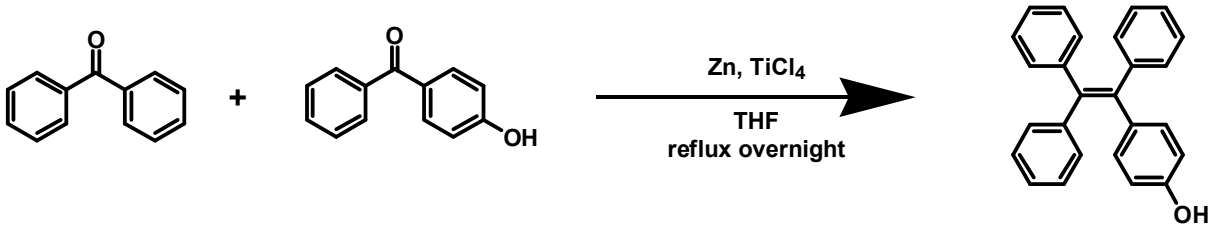


Figure S1. ^{1}H NMR spectra of (a) Boc-*L,L*-diphenylalanine methyl ester (BocPhePheOMe), (b) *L,L*-diphenylalanine methyl ester (NH_2PhePheOMe), and *N*-acryloyl-*L,L*-diphenylalanine methyl ester (APhePheOMe) in DMSO-d_6.

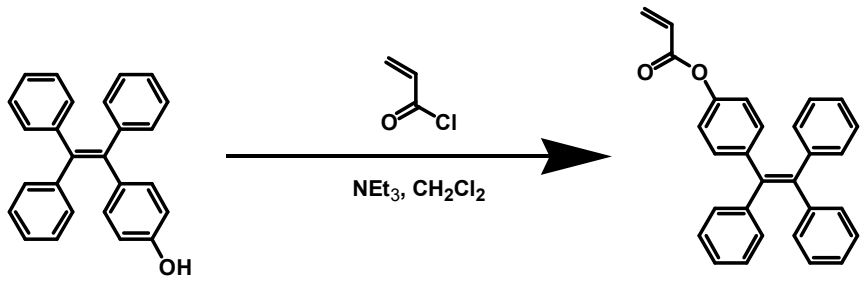
Synthesis of 4-(1,2,2-triphenylvinyl)phenol (TPEOH)[7]



TPEOH

TPEOH was synthesized according to a reported method[7] (yield 35%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25-6.95 (m, 15H: -phenyl), 6.91–6.85 (d, 2H: -phenyl), 6.62–6.54 (d, 2H: -phenyl), 4.70 (d, 1H: -O*H*).

Synthesis of 4-(1,2,2-triphenylvinyl)phenyl acrylate (ATPE)[4,8]



TPEOH ATPE

TPEOH (2.0 g, 5.74 mmol) was dissolved in dry dichloromethane (40 mL). After adding 3.0 equiv. of triethylamine (2.4 mL, 17.2 mmol) to the solution, 2.0 equiv. of acryloyl chloride (0.93 mL, 11.5 mmol) were added drop wise at 0°C. The mixture was then stirred at room temperature for 4 h. The ammonium salt was filtered off and the solvent was evaporated. The crude product was purified on a silica gel using solid column chromatography with dichloromethane/hexane (2:1 vol/vol) as eluting solvent to give ATPE as white solid (2.31 g, 93%). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25–7.01 (m, 17H: -phenyl), 6.89-6.86 (d, 2H: -phenyl), 6.54 (d, 1H: -C*H*=CH_2), 6.27 (dd, 1H: -CH=CH_2), 5.97 (d, 1H: -CH=CH_2).

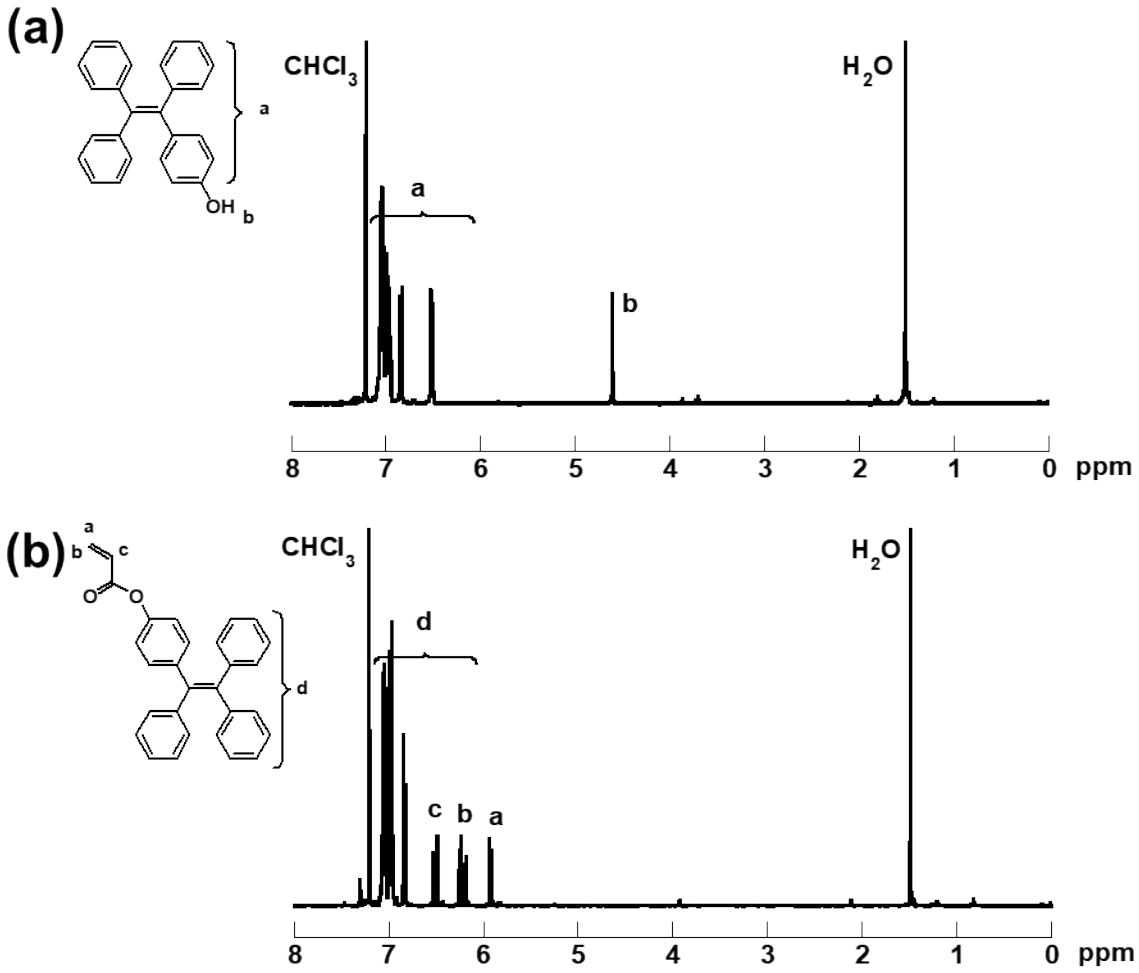


Figure S2. ^{1}H NMR spectra of (a) TPEOH and (b) ATPE in $CDCl_3$.

Synthesis of P(APhePheOH-*co*-ATPE)

A representative example (APhePheOH:ATPE feed ratio = 1/1) is as follows: APhePheOH (0.200 g, 0.545 mmol), ATPE (0.220 g, 0.546 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (7.96 mg, 0.0218 mmol), AIBN (1.80 mg, 0.0109 mmol), and dehydrated DMF (1.67 mL) were placed in a dry glass ampule equipped with a magnetic stirring bar, and the solution was degassed by three freeze-evacuate-thaw cycles. After sealing the ampule by flame under vacuum, the mixture was stirred at 60 °C for 24 h. Monomer conversion (APhePheOH) was determined by ^{1}H NMR of the crude product by comparing the integral comparison of relative area of the vinyl proton of APhePheOH unit (1H) (δ 5.56-5.49 ppm) to the methylene protons (2H) of APhePheOH unit (δ 4.81-4.25 ppm) in the monomer and polymer, using the equation 1 (x represents the monomer conversion).

$$\frac{\text{Integral at 5.56 - 5.49 ppm}}{\text{1H}} : \frac{\text{Integral at 4.81 - 4.25}}{\text{2H}} = 1 - x : x \quad (1)$$

Similarly, the monomer conversion (ATPE) was determined by ^{1}H NMR of the crude product by comparing the integral comparison of relative area of the vinyl proton of ATPE unit (1H) (δ 6.47-6.42 ppm) relative area of the aromatic protons of APhePheOH unit (10H), and ATPE unit (19H) (δ 7.86-6.80 ppm), using the equation 2 (x represents the monomer conversion).

$$\frac{\text{Integral at 6.47 - 6.42 ppm}}{\text{1H}} : \frac{\text{Integral at 7.86 - 6.80}}{\text{19H}} \times \frac{[\text{ATPE}]}{[\text{APhePheOH}] + [\text{ATPE}]} = 1 - x : x \quad (2)$$

After the copolymerization, the reaction mixture was poured into diethyl ether/hexane (2:1 = v/v) and the precipitate was collected by filtration. The product was dried in vacuo at room temperature to afford white solid; yield 74 % (0.31 g). ^{1}H NMR (400MHz, DMSO-d_6): δ 9.15-8.18 (broad, 2H: -N*H* in APhePheOH), 7.78-6.65 (broad, 10H: -phenyl in APhePheOH and 19H: -phenyl in ATPE), 5.00-4.22 (broad, 2H: -NHC*H*CH_2-phenyl and -NHC*H*COOH), 3.18-2.46 (broad, 4H, -CH_2-phenyl), 2.27-0.70 (broad, C*H* and CH_2 in the polymer main chain) ppm. The APhePheOH/ATPE composition was determined using ^{1}H NMR spectroscopy by comparison of relative area of the aromatic protons of APhePheOH unit (10H), and ATPE unit (19H) (δ 7.86-6.80 ppm), to the methylene protons (2H) of APhePheOH unit (δ 4.81-4.25 ppm), using the equation 3.

$$\frac{19 - 9x}{2x} = \frac{\text{Integral at 7.86 - 6.80 ppm}}{\text{Integral at 4.81 - 4.25 ppm}} \quad (3)$$

where x represents the fraction of the APhePheOH and 1-x represents the fraction of ATPE, respectively. The ^{1}H NMR spectra of the crude and purified products are shown in Figures S3 and S4.

The APhePheOH/ATPE composition was determined by elemental analysis using equation 4.

$$\text{Nitrogen content (obsd)} = \frac{(\text{Nitrogen content (calcd) in APhePheOH/MW of APhePheOH}) \times x}{(1 - x) \times \text{MW of ATPE} + x \times \text{MW of APhePheOH}} \quad (4)$$

where nitrogen content (obsd) represents nitrogen content of the P(APhePheOH-*co*-ATPE) determined by elemental analysis.

The methylation of the APhePheOH unit in the copolymer was conducted by treating the

carboxylic acid groups using trimethylsilyldiazomethane as reported previously,[1] to afford P(APhePheOMe-*co*-ATPE), which was used for the SEC measurement. The methylated copolymer has an $M_{n,SEC}$ value of 8300, and a polydispersity index (M_w/M_n) of 1.24.

For the determination of reactivity ratios (r_1 and r_2), low conversion samples over a range of feed compositions (APhePheOH/ATPE = 10/90–90/10**)** were prepared under the same conditions by simply adjusting the polymerization time (Table S1).

Synthesis of P(APhePheOMe-*co*-ATPE)

APhePheOMe (0.24 g, 0.63 mmol), ATPE (0.26 g, 0.64 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (9.11 mg, 0.025 mmol), AIBN (1.97 mg, 0.012 mmol), and dehydrated DMF (2.00 mL) were placed in a dry glass ampule, and the polymerization was conducted, according to the method describe above. The monomer conversions (APhePheOMe and ATPE) were determined by ^{1}H NMR of the crude product using equations 1 and 2.

The product was obtained as a white solid; yield 77 % (0.38 g). ^{1}H NMR (400MHz, DMSO-d_6): δ 9.30-8.05 (broad, 2H: -N*H* in APhePheOMe), 7.86-6.70 (broad, 10H: -phenyl in APhePheOMe and 19H: -phenyl in ATPE), 4.81-4.25 (broad, 2H: -NHC*H*CH_2-phenyl and -NHC*H*$COOCH_3$), 3.70 (broad, 3H: -COOCH_3 in APhePheOMe), 3.18-2.69 (broad, 4H,-CH_2-phenyl), 2.27-0.70 (broad, C*H* and CH_2 in the polymer main chain) ppm. The ^{1}H NMR spectra

of the crude and purified products are shown in Figures S5 and S6. The APhePheOMe/ATPE composition was determined using ^{1}H NMR spectroscopy and elemental analysis using similar procedures described for P(APhePheOH-*co*-ATPE). P(APhePheOMe-*co*-ATPE) was directly employed for SEC measurement, which has an $M_{n,SEC}$ of 9000, and a M_w/M_n of 1.39.

Instrumentation

The ^{1}H NMR (400 MHz) spectra were recorded using a JEOL JNM-ECX400 in DMSO-d_6 as a deuterated solvent at room temperature (the number of scan = 8). Chemical shifts are given as δ values in ppm, and calibrated using residual undeuterated solvent (2.50 ppm for DMSO-d_6) as internal reference. The number-average molecular weights and dispersities (M_n and M_w/M_n) were estimated by applying SEC at 40 °C using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors. The column set was as follows: four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limited molecular weight): α-M (13 μm, >1 × 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 of 1.0 mL/min using DMF containing 10 mM LiBr as the eluent. Polystyrene standards were employed for calibration. The elemental analysis was performed on a PerkinElmer 2400 II CHNS/O analyzer.

The circular dichroism (CD) was measured using a JASCO J-720 spectropolarimeter. The

ultraviolet–visible (UV–vis) and fluorescence spectra were recorded on a JASCO V-630BIO UV–vis spectrophotometer and a JASCO FP-6100 spectrofluorophotometer, respectively. Fluorescence quantum yields of solutions were determined relative to 9,10-diphenylanthracene (sublimation grade) in cyclohexane.[8] Transmission electron microscopy (TEM) measurements were performed on a JEOL TEM-2100F field emission electron microscope at an accelerating voltage of 200 kV. The sample for TEM observation was prepared by mounting a drop of the polymer solution on carbon-coated Cu grids and air-dried at room temperature. The samples were not stained. Field-emission scanning electron microscope (FE-SEM) measurements were performed on a Hitachi SU8000 microscope at an accelerating voltage of 1.0 kV. The sample prepared by mounting a drop of the polymer solution on carbon-coated Cu grid was employed without coating for SEM observation. Thermogravimetric analysis (TGA) with a SEIKO TG/DTA6200 was carried out at a heating rate of 10 °C/min.

Preparation of self-assembled structures

The copolymers were dissolved into THF as a good solvent to afford stock solutions at 20.0 mg/mL. For the preparation of the sample in THF/water (pH = 12) mixture (10/90 vol%, conc. = 1.0 mg/mL), 0.1 mL of the stock solution (20 mg/mL) was diluted with 0.9 mL of a distilled basic water (pH = 12). A slightly turbid suspension was detected after the addition the stock solution into water, and the sample was quickly mixed and then allowed to self-assemble for

24 h. For SEM, an aliquot (conc. = 2.0 mg/mL) was dropped on carbon-coated Cu grids at room temperature and allowed to dry in the air.

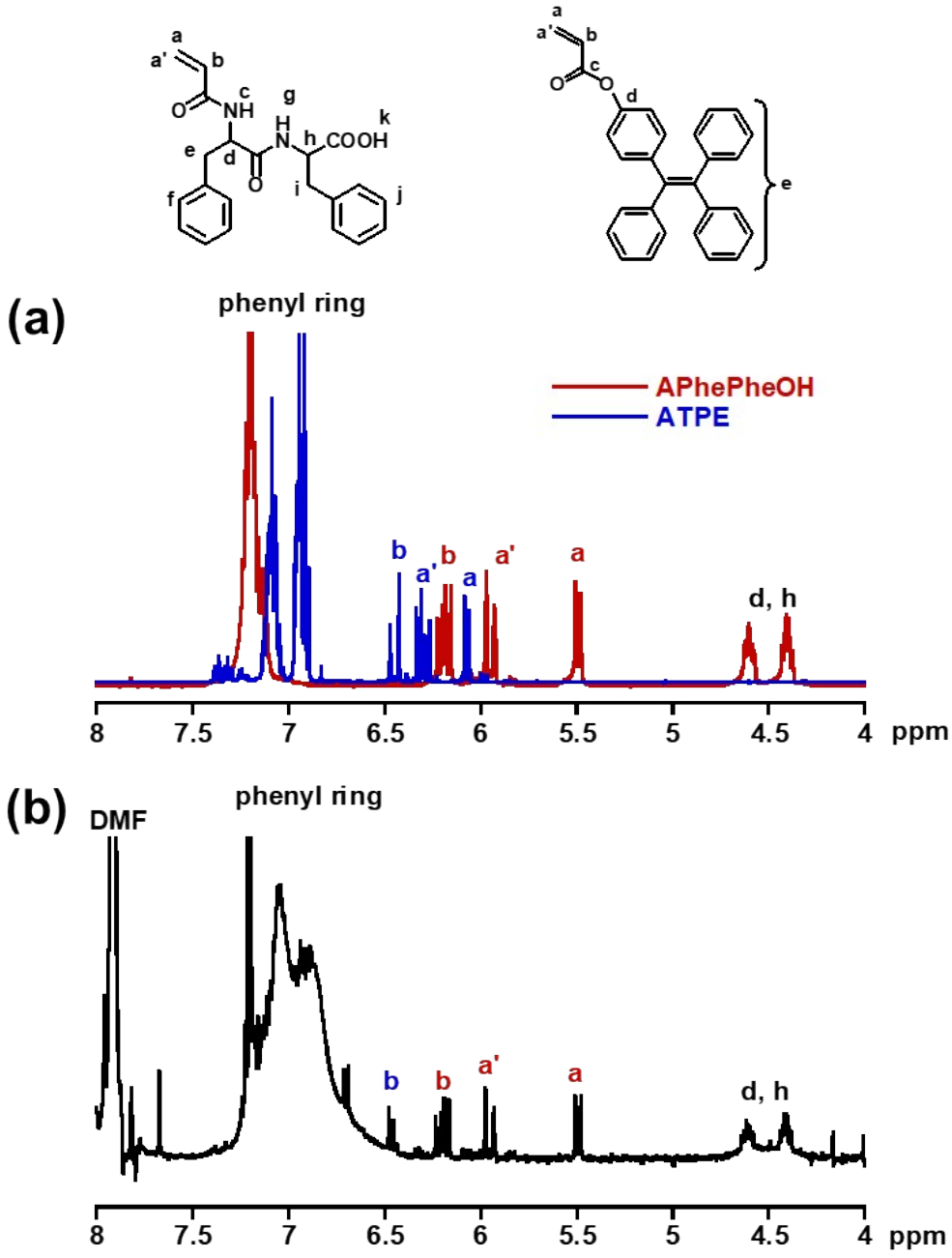


Figure S3. ^{1}H NMR spectra (DMSO-d_6) of (a) monomer mixture (APhePheOH/ATPE) and (b) crude product obtained by copolymerization of APhePheOH and ATPE at [I]/[CTA]/[APhePheOH]/[ATPE] =1/2/50/50 (Run 2 in Table 1).

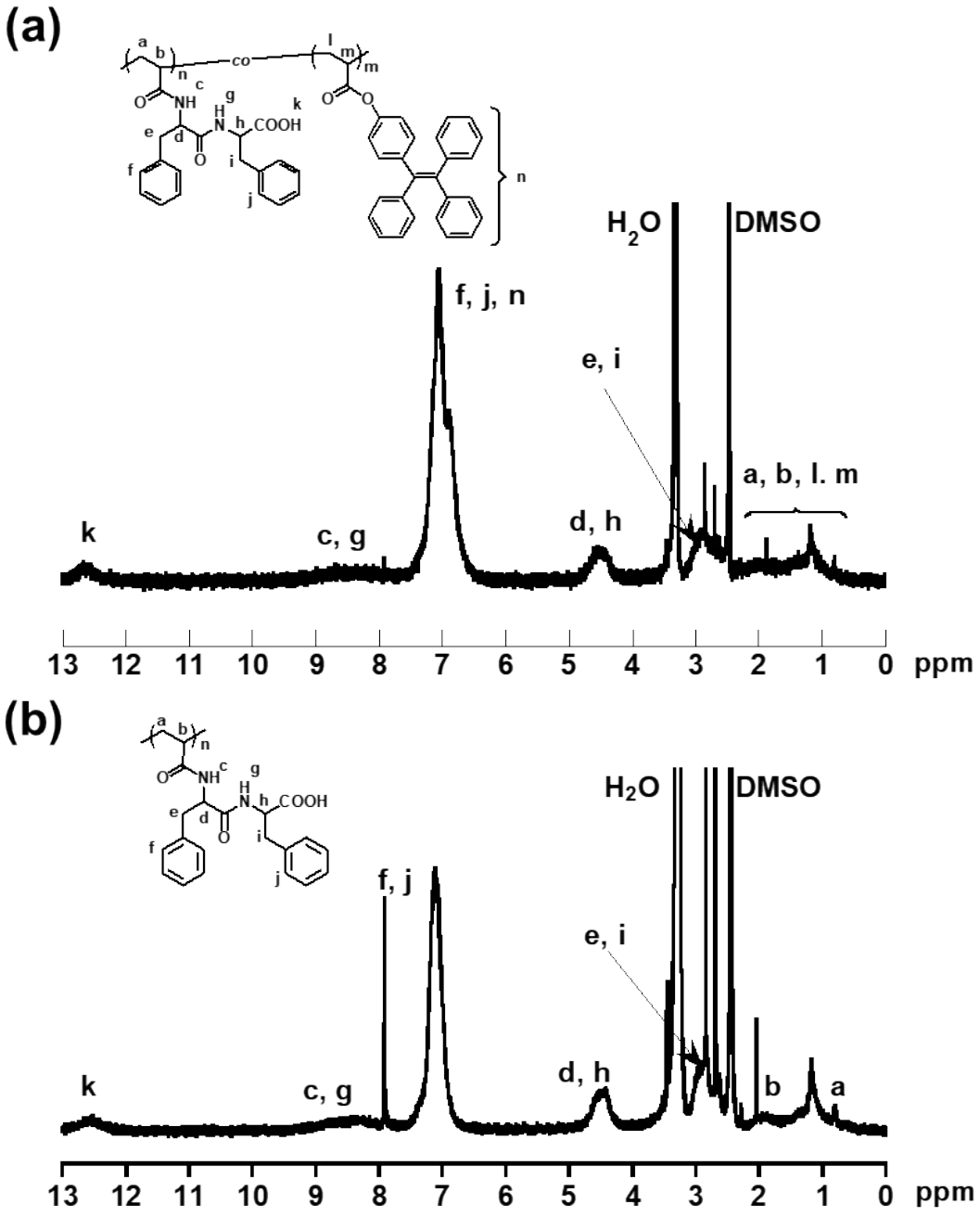


Figure S4. [1]H NMR spectra of (a) P(APhePheOH-*co*-ATPE) and (b) PAPhePheOH in DMSO-d_6.

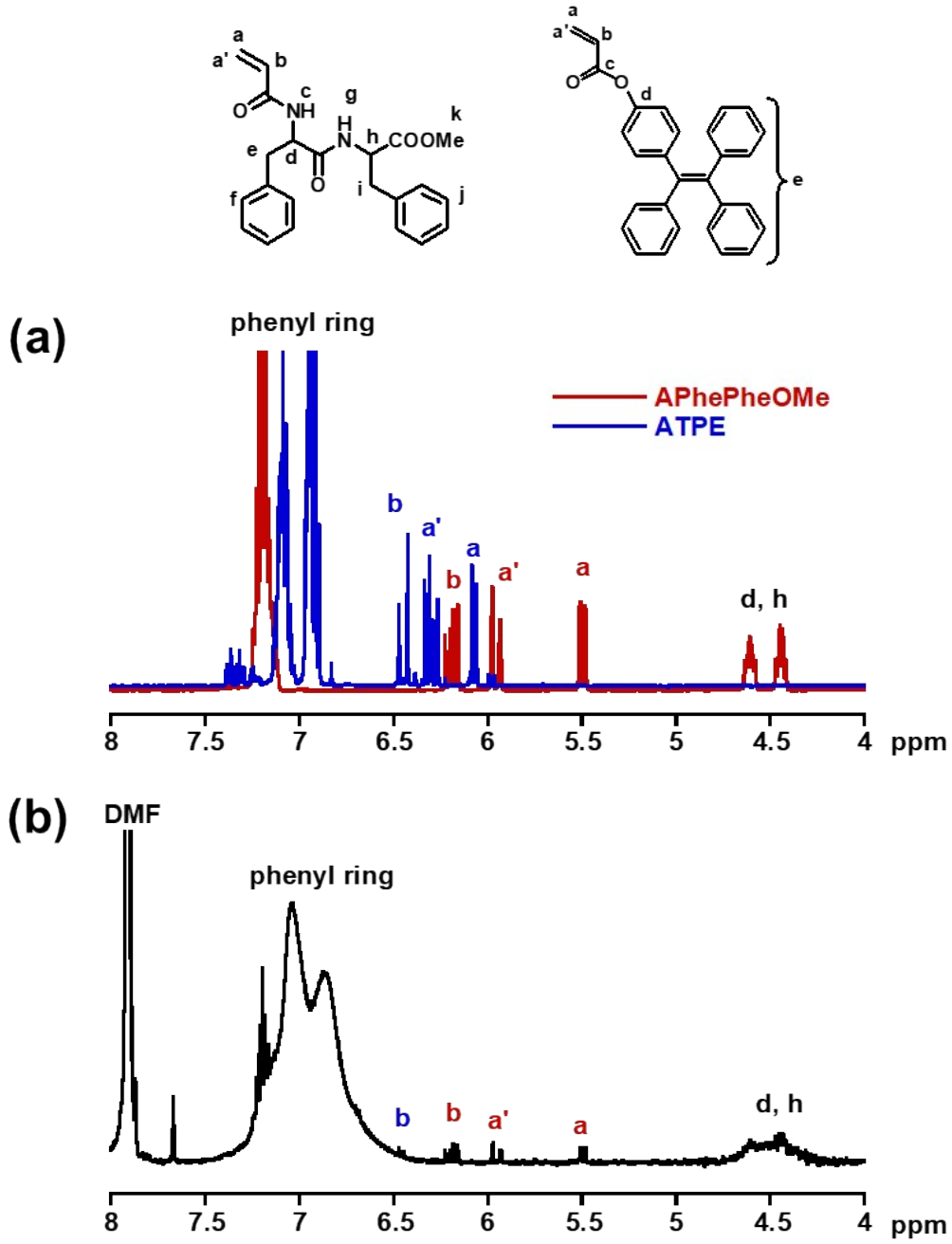


Figure S5 ^{1}H NMR spectra (DMSO-d_6) of (a) monomer mixture (APhePheOMe/ATPE) and (b) crude product obtained by copolymerization of APhePheOMe and ATPE at [I]/[CTA]/[APhePheOMe]/[ATPE] =1/2/50/50 (Run 1 in Table 2).

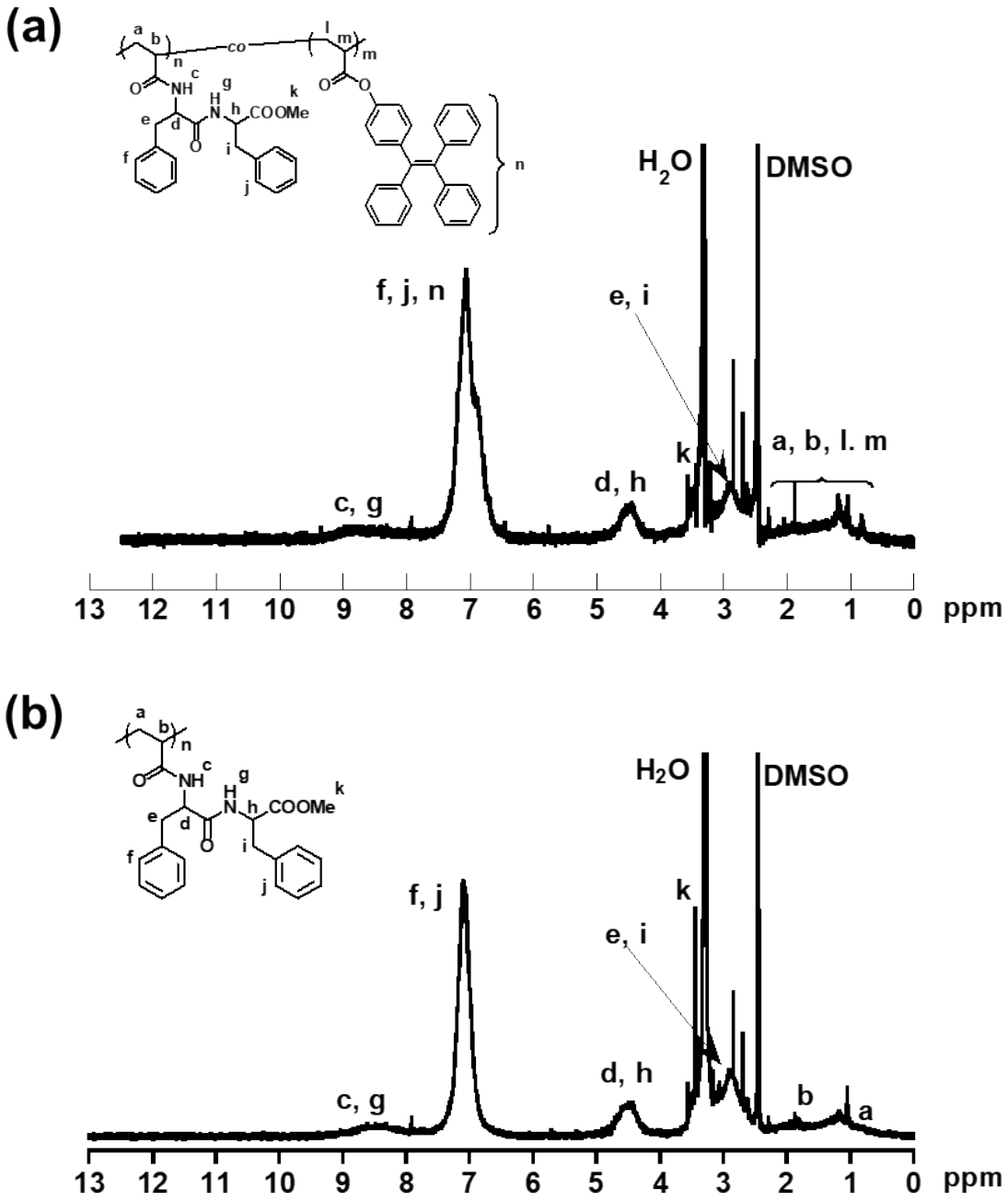


Figure S6. ^{1}H NMR spectra of (a) P(APhePheOMe-*co*-ATPE) and (b) PAPhePheOMe in DMSO-d_6.

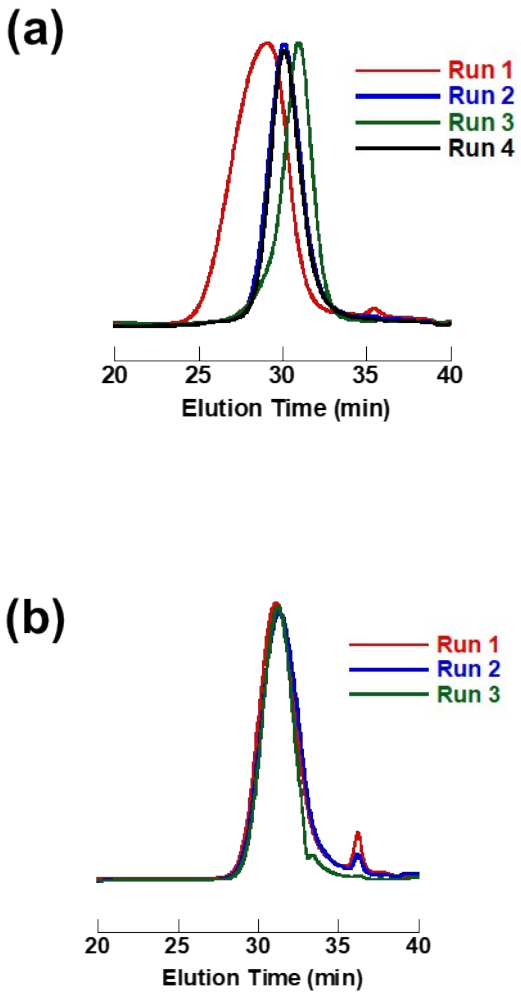


Figure S7. SEC curves of (a) methylated P(APhePheOH-*co*-ATPE)s and (b) P(APhePheOMe-*co*-ATPE)s (see Tables 1 and 2 for detailed polymerization conditions).

Table S1. RAFT copolymerization of APhePheOH and ATPE at different feed ratios.[a)]

Comonomer composition in the feed		Time (h)	Yield (%)[b)]	Copolymer composition[c)]	
APhePheOH (M1)	ATPE (M2)			APhePheOH (m1)	ATPE (m2)
10	90	4	2.7	1	99
25	75	3	1.2	7	93
50	50	2	8.2	40	60
75	25	2	2.9	68	32
90	10	2	6.8	80	20

[a)] Monomer concentration = 0.25 g/mL, [I]/[CTA]/[M] = 1/2/100, [M] = [APhePheOH]+[ATPE]; [I] = AIBN = 2,2′-azobis(isobutyronitrile). [b)]Diethyl ether/hexane (2:1 v/v)-insoluble fraction. [c)] Calculated using ^{1}H NMR spectroscopy in DMSO-d_6.

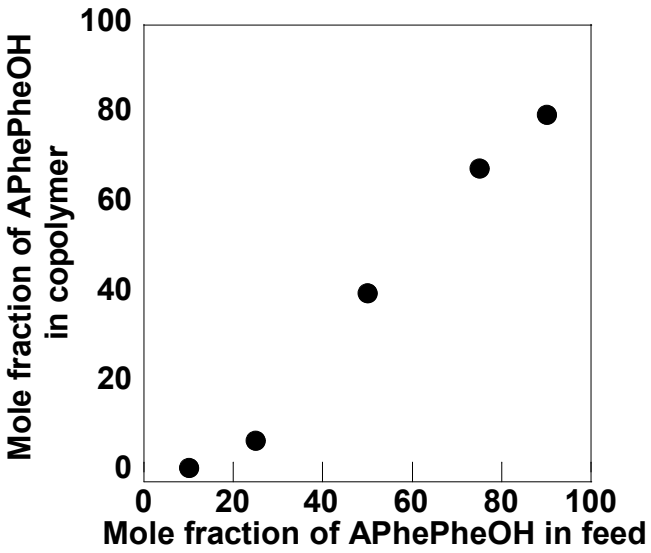


Figure S8. Composition plot of mole fraction of APhePheOH in the feed and mole fraction of APhePheOH in the copolymers obtained by RAFT copolymerization in DMF (Table S1).

Table S2. Solubilities of P(APhePheOH-*co*-ATPE)s and P(APhePheOMe-*co*-ATPE)s.

Solvent	P(APhePheOH)	P(APhePheOMe)	P(ATPE)	P(APhePheOH-*co*-ATPE) 56:44	P(APhePheOH-*co*-ATPE) 68:32	P(APhePheOH-*co*-ATPE) 86:14	P(APhePheOMe-*co*-ATPE) 47:53	P(APhePheOMe-*co*-ATPE) 73:27	P(APhePheOMe-*co*-ATPE) 88:12
MeOH	+	+	-	-	-	+	-	-	-
EtOH	+	+	-	-	-	+	-	-	-
HFIP	+	+	-	-	-	-	-	-	-
DMSO	+	+	-	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+
Acetone	+	+	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+	+	+
AcOEt	-	-	+	-	-	-	-	-	-
$CHCl_3$	-	+	+	-	-	-	+	+	+
DCM	-	+	+	-	-	-	+	+	+
Dioxane	-	-	+	-	-	-	-	-	-
H_2O (pH = 7)	-	-	-	-	-	-	-	-	-
H_2O (pH = 12)	+	-	-	-	-	+	-	-	-

+: soluble at r.t., -: insoluble at r.t., conc. = 1.0 mg/mL

Table S3. Results of elemental analysis of P(APhePheOH-*co*-ATPE)s

Entry[a)]	C (%)	H (%)	N (%)
Run 2	73.35	5.70	4.14
Run 3	71.17	5.74	5.09
Run 4	67.04	6.09	6.49

[a)] For detailed sample information, see Table 1.

Table S4. Results of elemental analysis of P(APhePheOMe-*co*-ATPE)s

Entry	C (%)	H (%)	N (%)
Run 1	77.11	6.18	3.39
Run 2	71.98	5.98	5.30
Run 3	69.24	6.47	6.44

[a)] For detailed sample information, see Table 2.

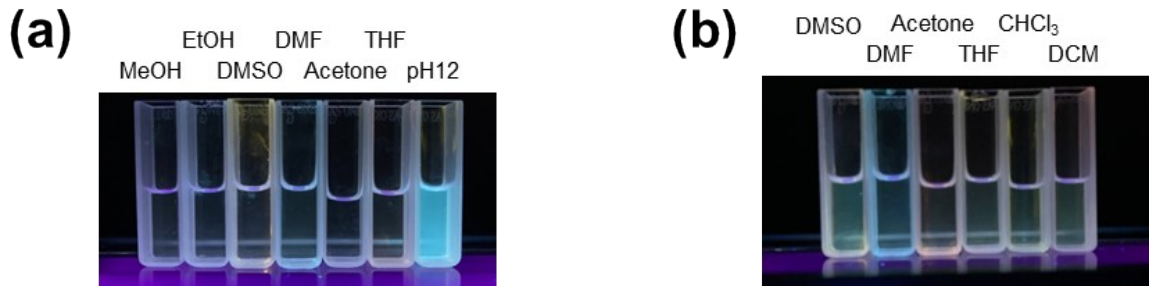


Figure S9. Photographs of copolymer solution under UV irradiation (λ_{ex} = 365 nm). (a) P(APhePheOH-*co*-ATPE) with high APhePheOH content (86%) and (b) P(APhePheOMe-*co*-ATPE) with high APhePheOMe content (88%) in various solvents (conc. = 0.3 mg/mL).

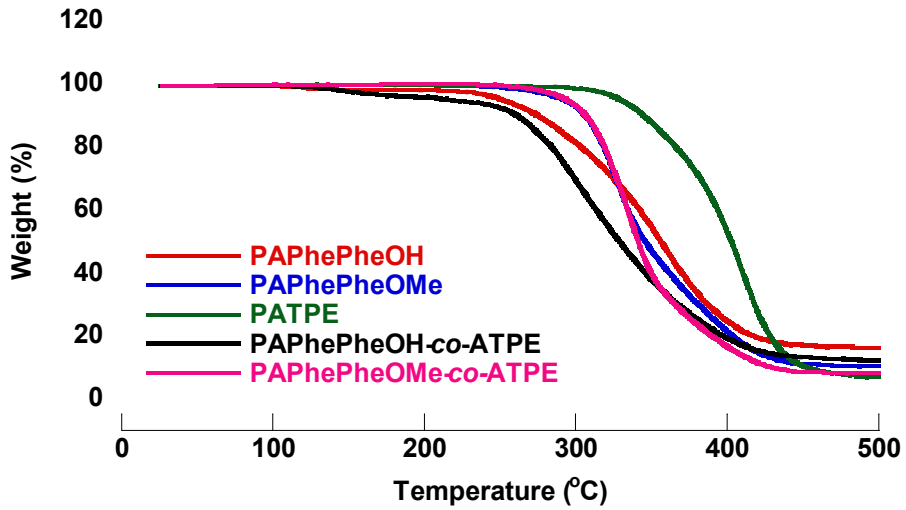


Figure S10. TGA curves of P(APhePheOH), P(APhePheOMe), P(ATPE), P(APhePheOH-*co*-ATPE), and P(APhePheOMe-*co*-ATPE).

Table S5. Thermal properties of P(APhePheOH), P(APhePheOMe), P(ATPE), P(APhePheOH-*co*-ATPE), and P(APhePheOMe-*co*-ATPE).

Sample	T_{d5} (°C)	T_{d10} (°C)
P(APhePheOH)	254.9	276.5
P(APhePheOMe)	294.6	307.2
P(ATPE)	331.8	346.2
P(APhePheOH-*co*-ATPE) (56:44)	227.5	262.9
P(APhePheOMe-*co*-ATPE) (47:53)	296.1	307.6

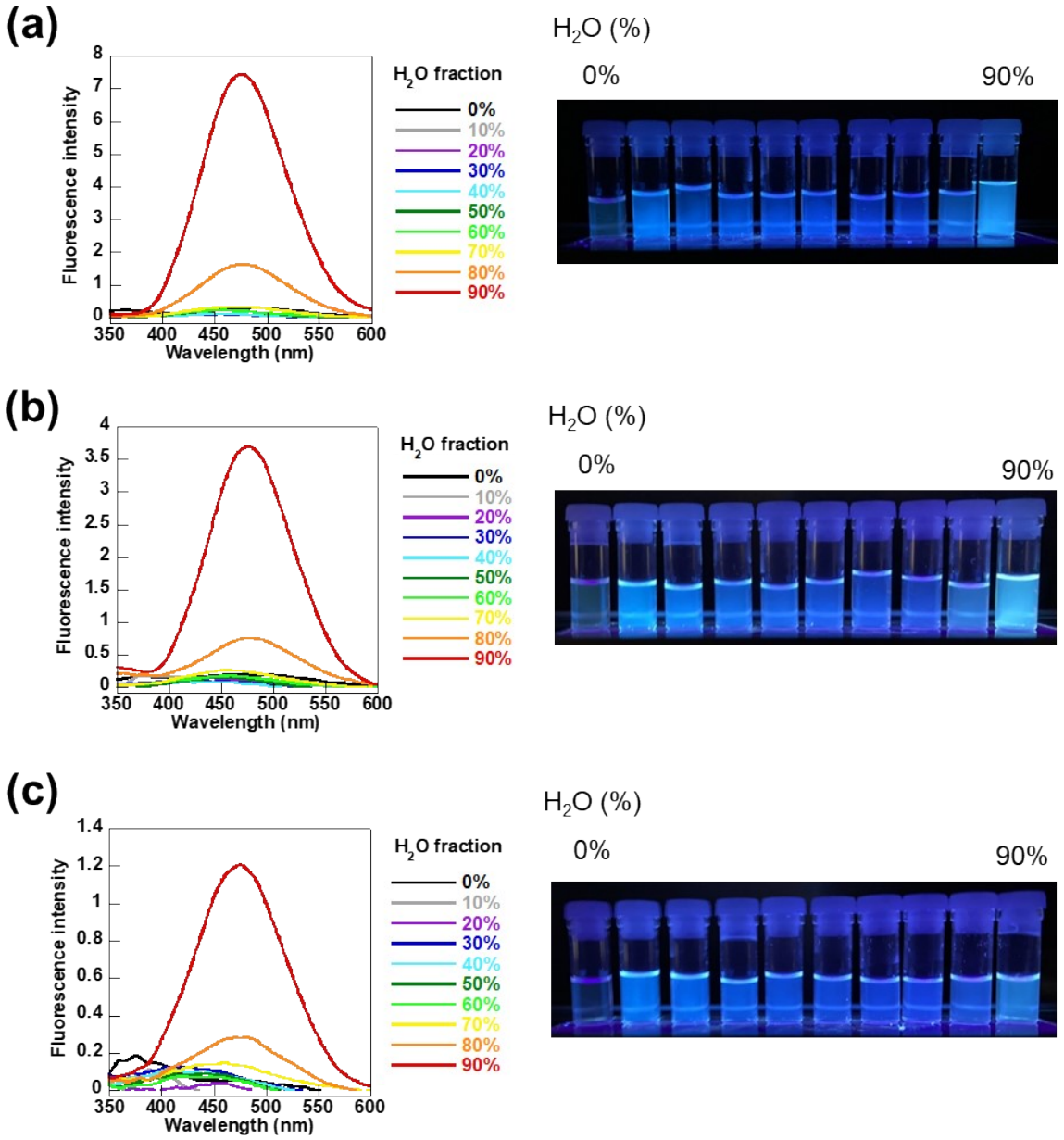


Figure S11. Fluorescence spectra of P(APhePheOH-*co*-ATPE)s with different comonomer compositions, APhePheOH:ATPE = (a) 56:44 (b) 68:32 (c) 86:14, in THF/water (pH = 12) mixtures (conc. = 0.03 mg/mL, λ_{ex} = 310 nm), and their photographs under UV irradiations (λ_{ex} = 365 nm).

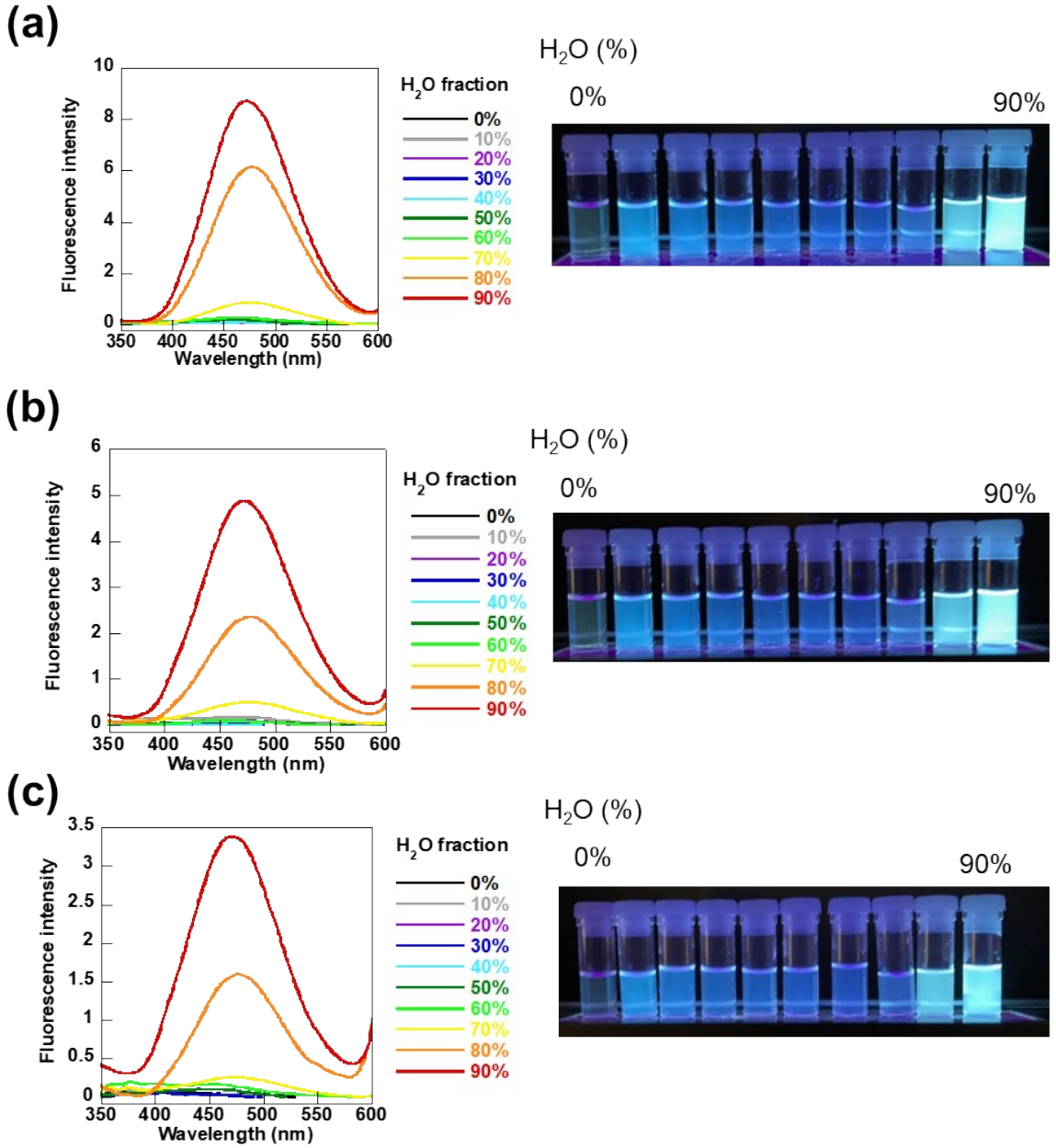


Figure S12. Fluorescence spectra of P(APhePheOMe-*co*-ATPE)s with different comonomer compositions, APhePheOMe:ATPE = (a) 47:53 (b) 73:27 (c) 88:12 in THF/water (pH = 12) mixtures (conc. = 0.03 mg/mL, λ_{ex} = 310 nm), and their photographs under UV irradiations (λ_{ex} = 365 nm).

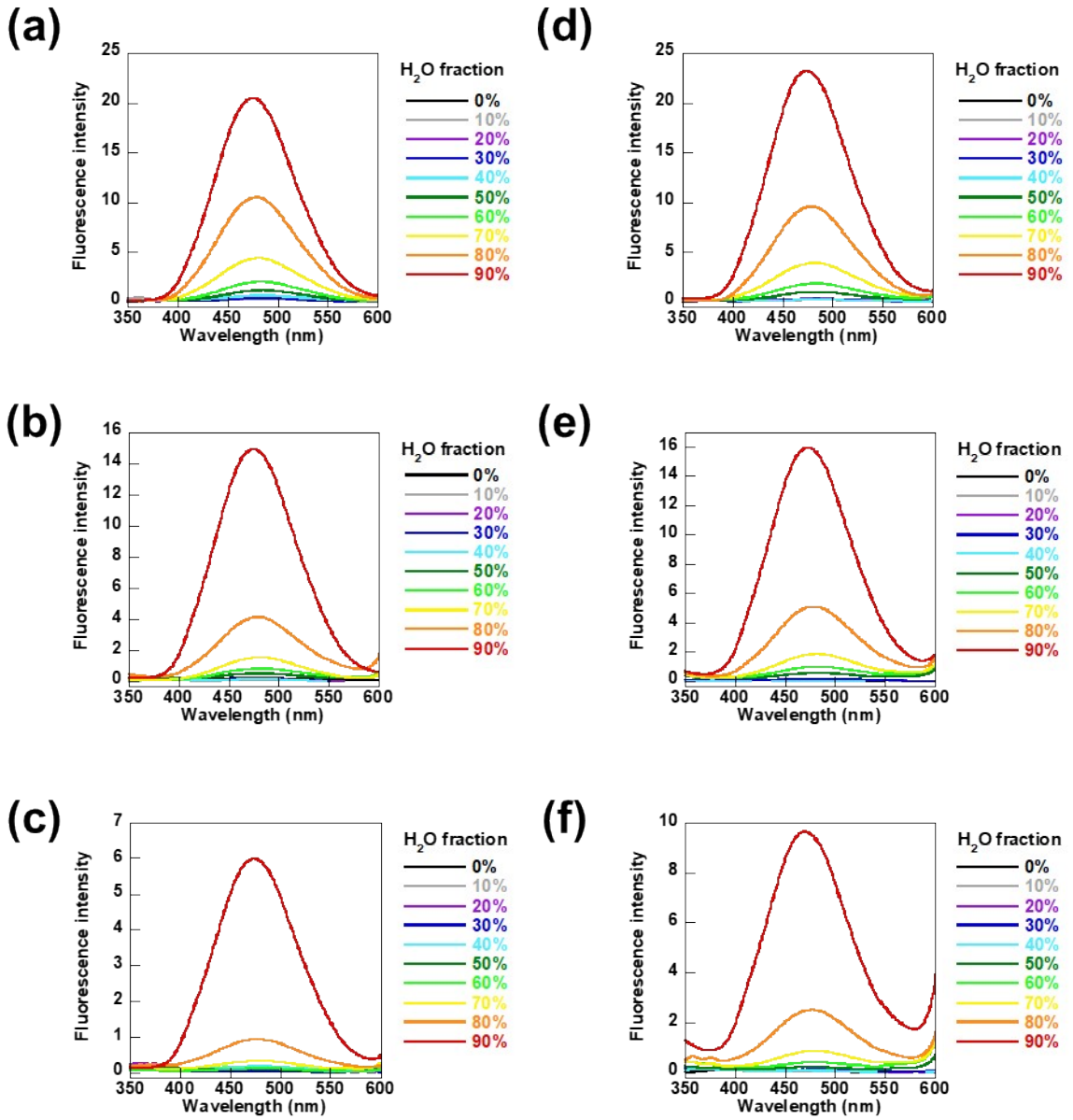


Figure S13. Fluorescence spectra of (a-c) P(APhePheOH-*co*-ATPE)s and (d-f) P(APhePheOMe-*co*-ATPE)s with different comonomer compositions, APhePheOH:ATPE = (a) 56:44, (b) 68:32, (c) 86:14, APhePheOMe:ATPE = (d) 47:53, (e) 73:27, (f) 88:12 in THF/water (pH = 7) mixtures (conc. = 0.03 mg/mL, λ_{ex} = 310 nm).

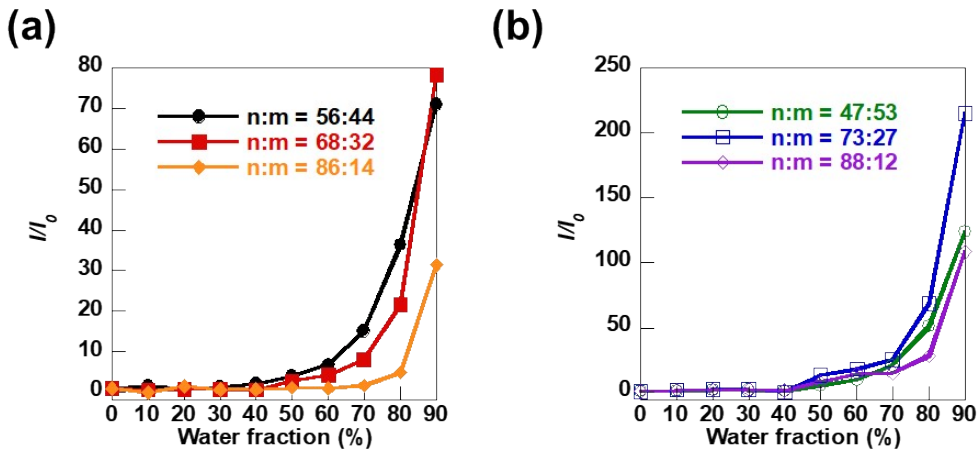


Figure S14. Plots of relative emission peak intensity (I/I_0) of (a) P(APhePheOH-*co*-ATPE)s and (b) P(APhePheOMe-*co*-ATPE)s at 480 nm versus water content in the THF/water (pH = 7) mixtures at different water fraction, where I = peak intensity and I_0 = peak intensity in pure THF (final conc. = 0.03 mg/mL).

Table S6. Fluorescence quantum yields of P(APhePheOH-*co*-ATPE)s and P(APhePheOMe-*co*-ATPE)s.

Sample	pH 7	pH 12
Poly(APhePheOH-*co*-ATPE) 56:44	3.2 %	1.2%
Poly(APhePheOH-*co*-ATPE) 68:32	4.3 %	1.1 %
Poly(APhePheOH-*co*-ATPE) 86:14	3.0 %	0.5 %
Poly(APhePheOMe-*co*-ATPE) 47:53	3.8 %	1.4 %
Poly(APhePheOMe-*co*-ATPE) 73:27	4.2 %	1.3 %
Poly(APhePheOMe-*co*-ATPE) 88:12	4.5 %	1.5 %

Conc. = 0.03 mg/mL, THF/water = 10/90 vol%.

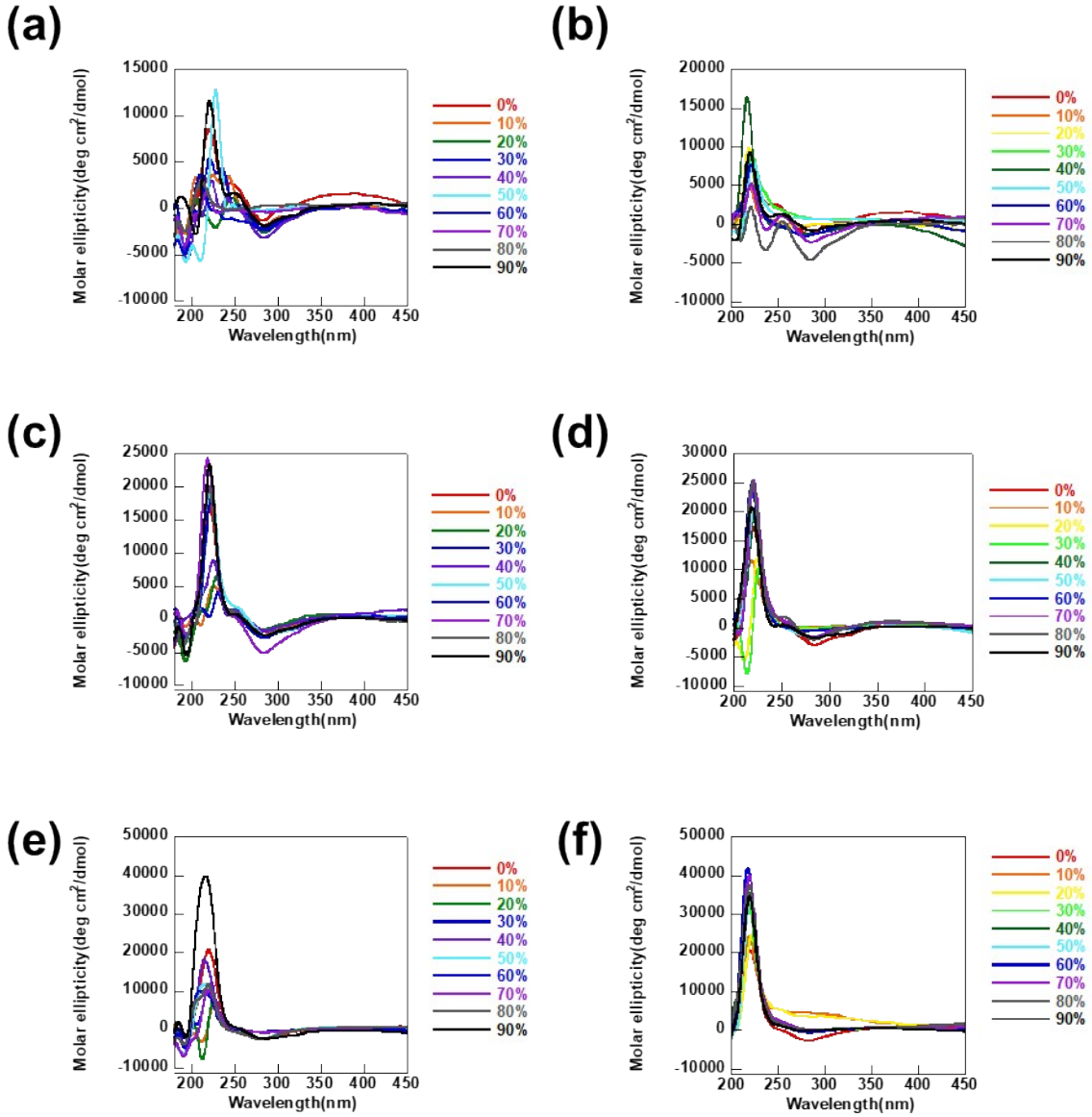


Figure S15. CD spectra of P(APhePheOH-*co*-ATPE)s with different comonomer compositions, APhePheOH:ATPE = (a, b) 56:44 (c, d) 68:32 and (e, f) 86:14, in THF/water mixtures with different water contents, (a, c, e) pH =7 and (b, d, f) pH = 12 (conc. = 0.03 mg/mL).

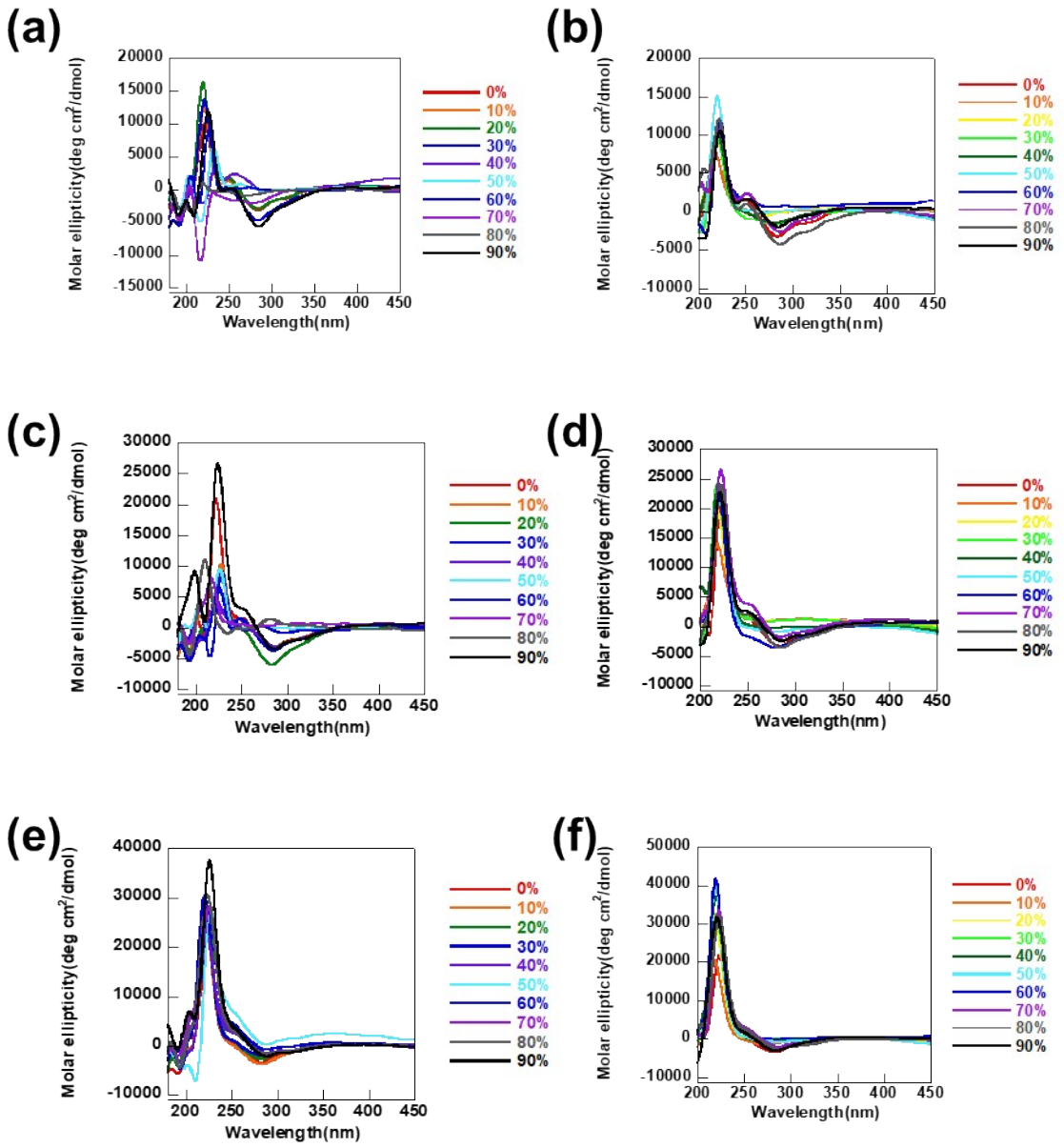


Figure S16. CD spectra of P(APhePheOMe-*co*-ATPE)s with different comonomer compositions, APhePheOMe:ATPE = (a, b) 47:53, (c, d) 73:27 (e, f) 88:12, in THF/water mixtures, (a, c, e) pH =7 and (b, d, f) pH = 12 (conc. = 0.03 mg/mL).

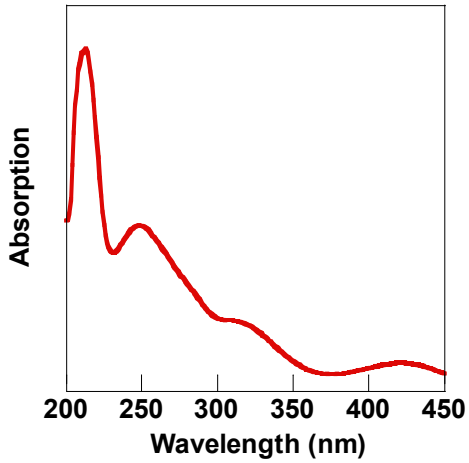


Figure S17. Representative example of UV-vis spectrum of P(APhePheOH-*co*-ATPE) in the presence of Thioflavin T (ThT) in THF/water (pH = 7) mixture (10/90 vol%, conc. = 0.03 mg/mL).

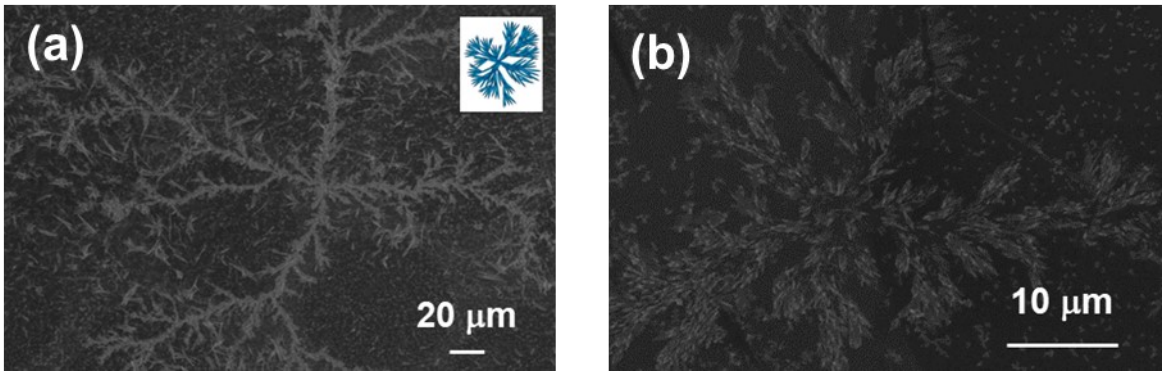


Figure S18. SEM images showing fractal structures of P(APhePheOH-*co*-ATPE)s with different comonomer compositions, APhePheOH:ATPE = (a) 86:14 and (b) 68:32, formed from THF/water (pH = 12) mixture (10/90 vol%, conc. = 2.0 mg/mL).

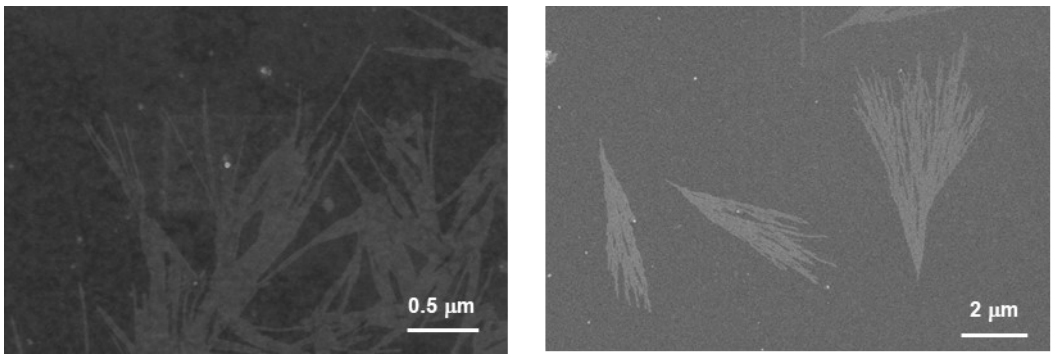


Figure S19. SEM images of P(APhePheOH-*co*-ATPE) assembled structures (APhePheOH:ATPE = 86:14) formed from THF/water (pH = 12) mixture (10/90 vol%, conc. = 1.0 mg/mL).

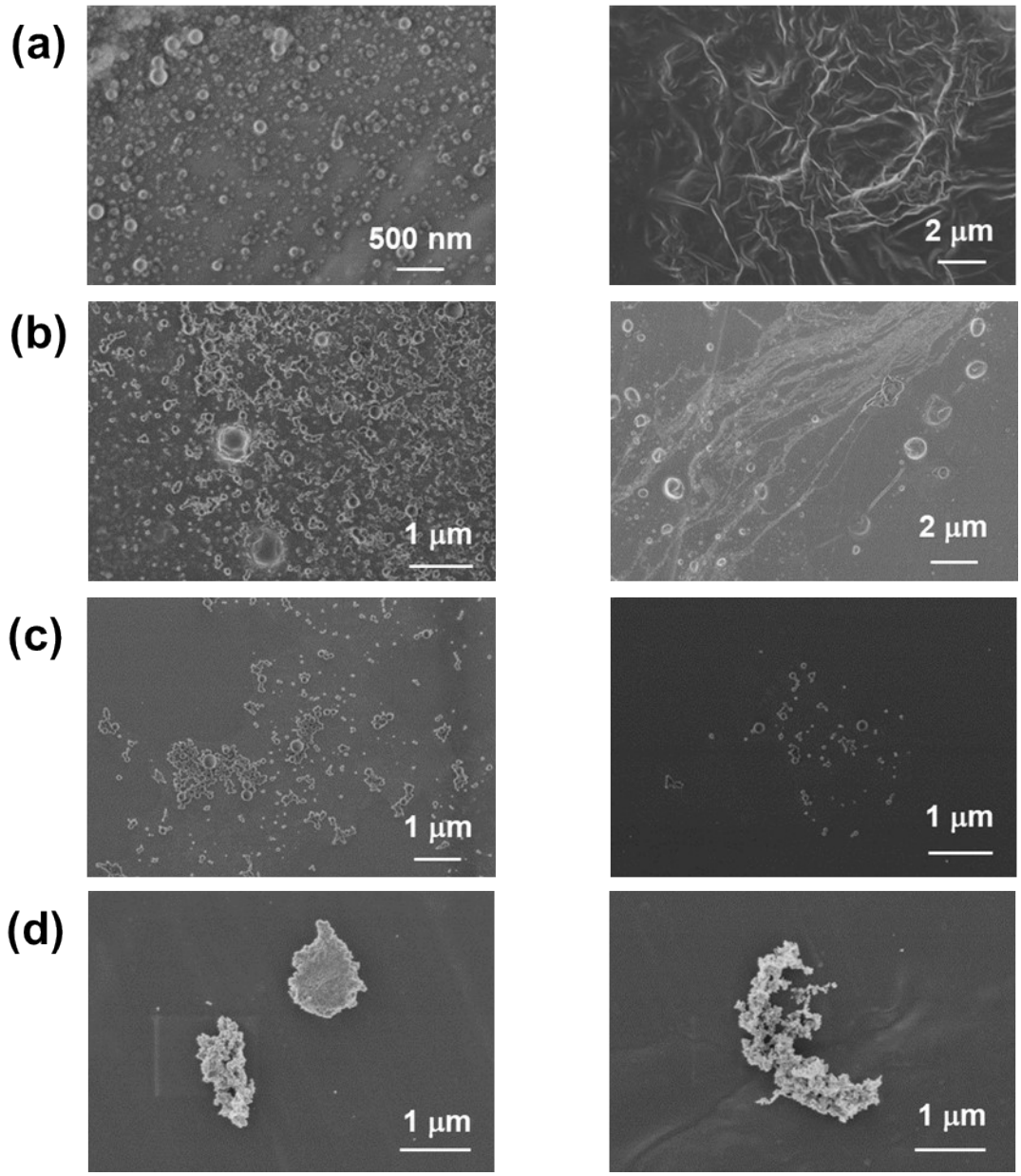


Figure S20. SEM images of P(APhePheOH-*co*-ATPE) with high APhePheOH content (86%) from THF/water mixtures (10/90 vol%), (a) THF/ water (pH = 10), (b) THF/phosphate buffer (pH = 7.4), (c) THF/water (pH = 5), and (d) THF/water (pH = 3) (conc. = 2.0 mg/mL).

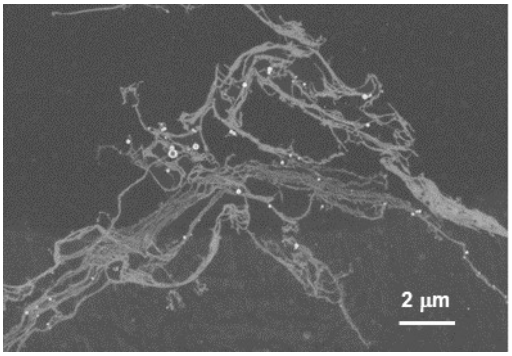


Figure S21. SEM image of P(APhePheOMe-*co*-ATPE) assembled structure (APhePheOMe:ATPE = 88:12) formed from THF/water (pH = 12) mixture (10/90 vol%, conc. = 1.0 mg/mL).

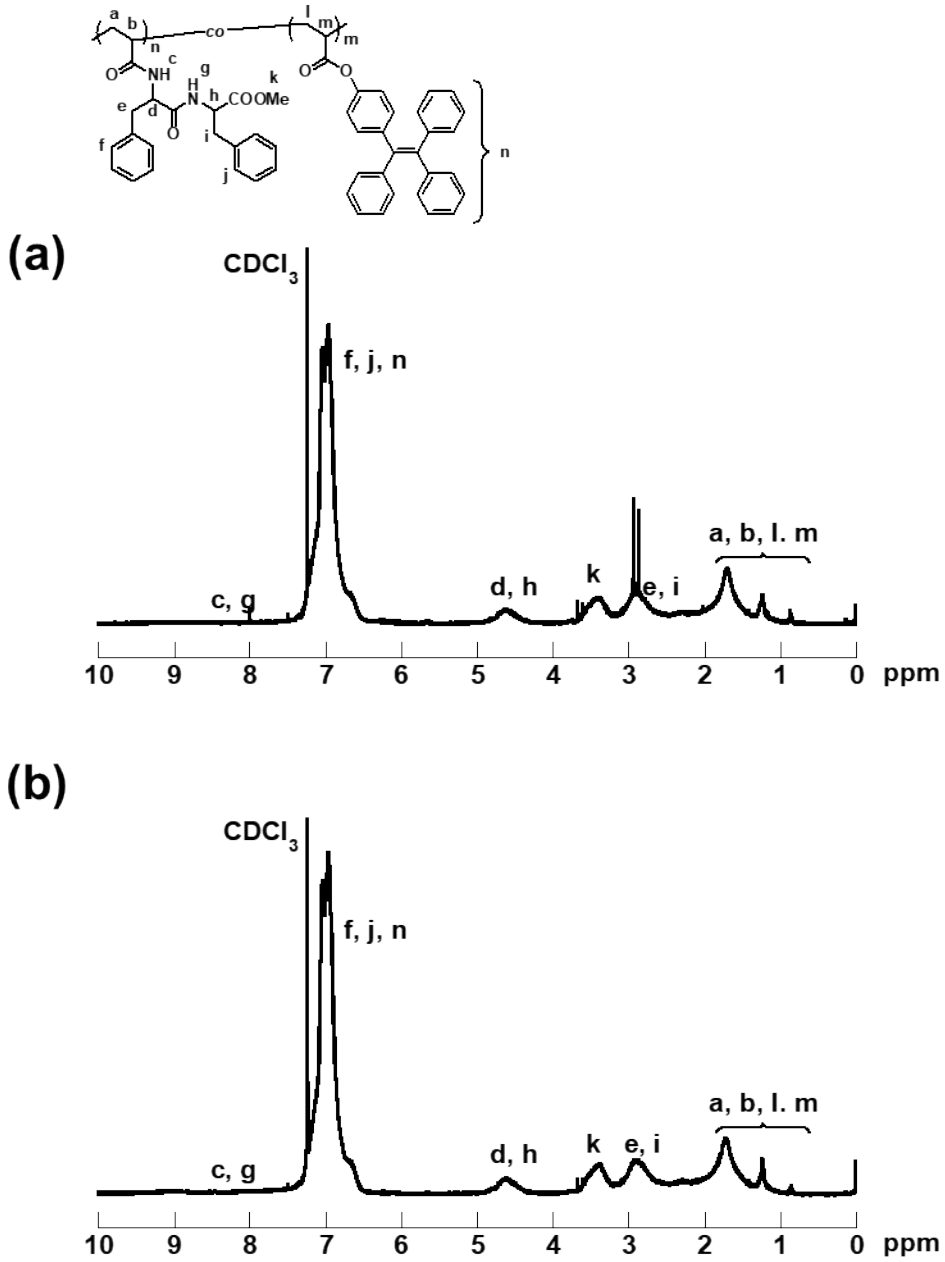


Figure S22. ^{1}H NMR ($CDCl_3$) of P(APhePheOMe-*co*-ATPE) (a) before and (b) after the treatment in THF/water (pH = 12). For the preparation of the treated sample, 40 mg of P(APhePheOMe-*co*-ATPE) was dissolved in 20 mL of THF/water (pH = 12) mixture (10/90 vol%), and then it was allowed to stand for room temperature for 1 day. After a part of the mixed solvent was removed under reduced pressure, the residue was reprecipitated into diether ether/hexane (2:1 = v/v) to obtain the treated sample.

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