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PiPo: random copolymer of *C*- and *N*-substituted glycine

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Supporting Information

Contents

Experimental

Materials

Sarcosine, lithium chloride, phenyl chloroformate (PCF), diphenyl carbonate (DPC), neopentylamine (NPA), hexafluoroisopropanol (HFIP), *N,N*-diisopropylethylamine (DiPEA), potassium trifluoroacetate (CF_3COOK), dicyclohexylcarbodiimide (DCC), dimethyl sulfoxide (DMSO, anhydrous, sealed under argon) and deuterated dimethyl sulfoxide (DMSO-d_6) were purchased from Energy Chemical (Shanghai, China). Benzylamine (BzA) was obtained from Shanghai Macklin Biochemical Co., Ltd. L-phenylalanine was bought from Adamas Reagent, Ltd. 2-Mercaptobenzothiazole, L-leucine, 2-chloro-1-methyl pyridinium iodide, methyl L-phenylalaninate hydrochloride, methyl sarcosinate hydrochloride, *N*-benzyloxycarbonyl-L-phenylalanine and *N*-benzyloxycarbonyl-sarcosine was purchased from Bidepharm (Shanghai, China). *N*-hydroxybenzotrizole (HOBt) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. 2-Methyl tetrahydrofuran was bought from J&K Scientific (Shanghai, China). *O-tert*-butyl-L-serine (OBLS) and N_ε-*tert*-butoxycarbonyl-L-lysine (BLL) was obtained from CS-Pharm Chemical Co., Ltd. Potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium hydroxide, triethylamine (TEA), hydrochloric acid, diethyl ether, methyl *tert*-butyl ether, toluene, ethyl acetate (EA), petroleum ether (PE), dichloromethane (DCM), dimethylformamide (DMF) and tetrahydrofuran (THF) were bought from Sinopharm Chemical Reagent Co., Ltd.

Measurements

Molecular weights and dispersites (*Đ*) were determined by size exclusion chromatography (SEC) in HFIP with 3 g/L CF_3COOK with a flow rate of 0.8 mL/min (pumped by a Waters 1515 isocratic HPLC pump) at 40 °C. Two Shodex KF series columns were used. A Waters-2414 refractive index detector was used to detect the polymer. Molecular weights were calibrated by commercial poly(methyl methacrylate) standards (Polymer Standards Services GmbH, Mainz, Germany).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DRX 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) in 25 °C with DMSO-d_6 as solvent and tetramethylsilane as internal reference.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) were collected on a Bruker (Leipzig, Germany) ultrafleXtreme MALDI-ToF mass spectrometer in the reflector mode. 2,5-Dihydroxybenzoic acid was invoked as matrix and

CF_3COOK was added as cationic agent.

Zeta potentials were determined using a Nano-ZS 90 Nano-sizer (Malvern Instruments Ltd). Each reported measurement was conducted for three repeating times.

Transmission electron microscopy (TEM) images were obtained using a HITACHI 7650 instrument.

(S)-1,3-Benzothiazol-2-yl-*O*-phenylthiocarbonate (Poc-MBT) Poc-MBT was synthesized according to the reported method.[1] Sodium carbonate (21.40 g, 0.2 mol) was added into a solution of 2-mercaptobenzothiazole (16.86 g, 0.1 mol) in 150 mL of THF. A solution of PCF (14 mL, 0.11 mol) in THF (50 mL) was added dropwise with vigorous stirring. After 1.5 h, the reaction mixture was filtrated, and the filtrate was evaporated under reduced pressure. The crude product was recrystallized in methanol and PE to get 11.5 g of product as white, needle-like crystal. The yield was 40.0%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.35-7.44 (m, 3H), 7.48-7.55 (m, 3H), 7.57-7.63 (m, 1H), 8.08 (d, 1H, J = 7.78 Hz), 8.21 (d, 1H, J = 7.71 Hz). ^{13}C NMR (DMSO-d_6): δ = 121.37, 122.18, 122.74, 126.08, 126.86, 127.16, 129.95, 136.07, 150.43, 141.50, 156.42, 164.96. Single crystal X-ray diffraction in CCDC 2106569 and the materials in Supporting Information.

***N*-phenyloxycarbonyl-sarcosine (Sar-NPC)** Lithium chloride (14.07 g, 0.25 mol) was added into a solution of sarcosine (22.29 g, 0.25 mol) and potassium hydroxide (10.69 g, 0.25 mol) in methanol (250 mL). The mixture was stirred to dissolve. A solution of 53.76 g of DPC (0.25 mol) in 150 mL of THF was added dropwise to the mixture. After vigorously stirred for 1.5 h, the reaction slurry was concentrated under reduced pressure. The pH was adjusted to 3 by 1 mol/L hydrochloric acid. The aqueous solution was washed by once of 500 mL and twice of 300 mL EA. The organic phase was collected, dried by anhydrous magnesium sulfate, filtrated and evaporated under reduced pressure to get crude product which was purified by chromatography (a gradient eluent EA:PE = 1:5-1:1) to obtain Sar-NPC as light-yellow viscous liquid (26.05 g, yield: 49.8%). ^{1}H NMR (DMSO-d_6): δ = 3.02 (d, 3H, J = 57.2 Hz), 4.08 (d, 2H, J = 48.7 Hz),7.00-7.47 (m, 5H), 12.90 (s, 1H). ^{13}C NMR (DMSO-d_6): δ = 35.85, 50.46, 121.68, 125.24, 129.24, 151.10, 154.24, 170.88.

***N*-phenyloxycarbonyl-L-phenylalanine (L-Phe-NPC)** A suspension of L-phenylalanine (16.52 g, 0.1 mol) and PCF (10.2 mL, 0.1 mol) in 250 mL of EA was heated at 45 °C for 48 h. The reaction mixture was filtrated, evaporated under reduced pressure, and recrystallized in

toluene and PE to get 5.69 g of product as white solid. The yield was 20.0%. ^{1}H NMR (DMSO-d_6): δ = 2.90-3.12 (m, 2H), 4.22 (m, 1H), 6.94-7.46 (m, 10H), 8.17 (d, 1H, J = 8.26 Hz), 12.86 (s,1H).

***N*-phenyloxycarbonyl-N_ε-*tert*-butoxycarbonyl-L-lysine (BLL-NPC)** BLL-NPC was synthesized as L-Phe-NPC except 24.62 g of BLL (0.1 mol) and 12.6 mL of PCF (0.1 mol) were used. Crude product was purified by chromatography (a gradient eluent EA:PE = 1:5-1:1) to give 8.45 g of BLL-NPC as light salmon colored sticky solid (yield = 23.1%). ^{1}H NMR (DMSO-d_6): δ = 1.16 (s, 9H), 3.63 (m, 2H), 4.15 (m, 1H), 6.95-7.46 (m, 5H), 7.85 (d, 1H, J = 8.17 Hz), 12.80 (s, 1H).

***N*-phenyloxycarbonyl-*O*-*tert*-butyl-L-serine (OBLS-NPC)** OBLS-NPC was synthesized as L-Phe-NPC except 9.70 g of OBLS (0.06 mol) and 7.6 mL of PCF (0.06 mol) were used. Crude product was recrystallized in diethyl ether and PE to get 1.95 g of product as white solid. The yield was 11.6%. ^{1}H NMR (DMSO-d_6): δ = 1.16 (s, 9H), 3.63 (m, 2H), 4.15 (m, 1H), 6.95-7.46 (m, 5H), 7.85 (d, 1H, J = 8.17 Hz), 12.80 (s, 1H).

***N*-phenyloxycarbonyl-L-leucine (L-Leu-NPC)** 6.56 g of L-leucine (0.05 mol) and sodium bicarbonate (4.20 g, 0.05 mol) were dissolved in 80 mL of water. The solution was heated to 50 °C, followed by a solution of Poc-MBT (15.80 g, 0.055 mol) in 250 mL of THF. The mixture was refluxed and vigorously stirred for 2 h, then diluted with 240 mL of 20% aqueous sodium bicarbonate and concentrated under reduced pressure to remove THF. The obtained slurry was filtrated, washed by EA (250 mL×3), acidified to pH<3 with 12 mol/L hydrochloric acid, and extracted by EA (250 mL×3). The latter organic solution was collected, washed by brine twice, dried by anhydrous magnesium sulfate, filtrated and evaporated under reduced pressure to get product as colorless syrupy liquid (9.94 g, yield = 79.1 %). ^{1}H NMR (DMSO-d_6): δ = 0.91 (dd, 6H, J = 6.65 Hz), 1.47-1.67 (m, 2H), 1.73 (m, 1H), 4.01 (m, 1H), 7.08-7.41 (m, 5H), 8.09 (d, 1H, J = 8.06 Hz), 12.68(s, 1H).

The Phe-Phe dipeptide (methyl *N*-(benzyloxycarbonyl-L-phenylalanyl)-L-phenylalanate) *N*-benzyloxycarbonyl-L-phenylalanine (3.02 g, 10 mmol) was dissolved in 10 mL of DMF, DCC (2.48 g, 12 mmol) and HOBt (1.08 g, 8 mmol) were added respectively under ice bath. After stirring for 10 min, mixture of DMF solution (10 mL) of methyl L-phenylalanate hydrochloride (1.88 g, 10.5 mmol) and TEA (1.46 mL, 10.5 mmol) was added. The reaction

mixture was set aside overnight with removing ice bath, the separated with 50 mL of water and 50 mL of EA. The organic layer was washed with saturated sodium bicarbonate solution and saturated sodium chloride solution successively, and evaporated under reduced pressure. The crude product was purified by chromatography (a gradient eluent EA:PE = 1:1 to pure EA) to obtain the product (3.51 g, yield = 76.2 %).

The Phe-Sar dipeptide (methyl *N*-(benzyloxycarbonyl-L-phenylalanyl)-sarcosinate) *N*-benzyloxycarbonyl-L-phenylalanine (3.02 g, 10 mmol), methyl sarcosinate hydrochloride (1.46 g, 10.5 mmol) and 2-chloro-1-methyl pyridinium iodide (3.34 g, 13 mmol) were added into 54 mL of 2-methyl tetrahydrofuran. DiPEA (3.90 g, 30 mmol) was added into the mixture, and the reaction mixture was aged for 4 h by stirring in room temperature. 45 mL of water was added to quench the reaction, and the organic phase was washed by sodium hydroxide aqueous solution (0.1 mol/L, 45 mL), hydrochloric acid (0.15 mol/L, 30 mL) and 2 times of water (30 mL) successively, and evaporated under reduced pressure. The crude product was purified by chromatography (a gradient eluent EA:PE = 2:3 to pure EA) to obtain the product (2.47 g, yield = 64.3 %). The Sar-Phe and Sar-Sar dipeptides were synthesized according to the same procedure.

A typical polymerization towards PiPo

All polymerizations were performed using Schlenk technique under anhydrous condition. Sar-NPC (0.21 g, 1 mmol) and DiPEA (0.02 g, 0.16 mmol) were dissolved in the reaction tube with 1 mL of anhydrous DMSO. A solution of L-Phe-NPC (0.28 g, 1 mmol) in 1 mL of DMSO was added by syringe. After adding DMSO solution of NPA, the reaction tube was sealed and placed in an oil bath at 60 °C for 48 h. The reaction mixture was cooled to room temperature and precipitated by methyl *tert*-butyl ether. Polymers were isolated after centrifugation and dried in vacuum.

Measurement of polymerization kinetics

Sar-NPC (10.7 mg, 0.05 mmol), L-Phe-NPC (14.4 mg, 0.05 mmol), DiPEA solution in DMSO-d_6 (50 μL, 0.16 mol/L) and NPA solution in DMSO-d_6 (30 μL, 0.033 mol/L) were added in 0.6 mL of DMSO-d_6 successively. The solution was moved into an NMR tube and placed in an oil bath at 60 °C. ^{1}H NMR spectra were recorded before heat and every 1 h when heated.

Measurement of monomer reactivity ratios

Different portions of Sar-NPC (0.13 mol/L), DiPEA (0.02 mol/L), L-Phe-NPC (0.15 mol/L) and NPA (0.05 mol/L) solution in DMSO-d_6 were added into NMR tubes. ^{1}H NMR spectra were measured before and after a one-hour heating at 60 °C.

Typical preparation procedure of nanoparticles

5 mg of PiPo sample was dissolved in 0.5 mL of HFIP. The solution of PiPo was added into 10 mL of water dropwise with vigorous stirring. The nanoparticle solution was obtained from dialysis against deionic water.

Table S1. Copolymerization of BLL-NPC with Sar-NPC with BzA as initiator [a].

Sample	[BLL-NPC]: [Sar-NPC] [b]	Yield	Polymer composition by NMR	M_n by NMR (kg/mol)	M_n by SEC (kg/mol)	$Đ$
7	1:5	73%	$P(BLL_{0.1}\text{-}r\text{-}Sar_{0.9})_{100}$	8.7	10.6	1.21
8	2:4	68%	$P(BLL_{0.27}\text{-}r\text{-}Sar_{0.73})_{88}$	10.0	9.7	1.22
9	3:3	69%	$P(BLL_{0.47}\text{-}r\text{-}Sar_{0.53})_{77}$	11.1	9.2	1.27
10	4:2	64%	$P(BLL_{0.63}\text{-}r\text{-}Sar_{0.37})_{76}$	12.9	10.2	1.36
11	5:1	75%	$P(BLL_{0.8}\text{-}r\text{-}Sar_{0.128})_{142}$	29.7	16.9	1.67

[a] Conditions: monomer (2.0 mmol overall), DMSO (3 mL), 60 °C for 48 h.

[b] [AA-NPC]:[BzA] = 100:1, [Sar-NPC]:[DiPEA] = 100:16.

Table S2. Copolymerization of OBLS-NPC with Sar-NPC with BzA as initiator [a].

Sample	[OBLS-NPC]: [Sar-NPC] [b]	Yield	Polymer composition by NMR	M_n by NMR (kg/mol)	M_n by SEC (kg/mol)	$Đ$
12	1:5	40%	$P(OBLS_{0.1}\text{-}r\text{-}Sar_{0.9})_{78}$	6.2	11.1	1.12
13	2:4	38%	$P(OBLS_{0.24}\text{-}r\text{-}Sar_{0.76})_{83}$	7.4	8.4	1.23
14	3:3	29%	$P(OBLS_{0.47}\text{-}r\text{-}Sar_{0.53})_{99}$	10.5	7.7	1.42
15	4:2	48%	$P(OBLS_{0.65}\text{-}r\text{-}Sar_{0.35})_{104}$	12.4	6.4	1.45
16	5:1	42%	$P(OBLS_{0.94}\text{-}r\text{-}Sar_{0.06})_{52}$	7.4	5.0	1.49

[a] Conditions: monomer (2.0 mmol overall), DMSO (3 mL), 60 °C for 48 h.

[b] [AA-NPC]:[BzA] = 100:1, [Sar-NPC]:[DiPEA] = 100:16.

Table S3. Copolymerization of L-Leu-NPC with Sar-NPC with BzA as initiator [a].

Sample	[L-Leu-NPC]: [Sar-NPC] [b]	Yield	Polymer composition by NMR	M_n by NMR (kg/mol)	M_n by SEC (kg/mol)	$Đ$
17	1:5	80%	$P(L\text{-}Leu_{0.1}\text{-}r\text{-}Sar_{0.9})_{110}$	8.4	12.2	1.10
18	2:4	78%	$P(L\text{-}Leu_{0.27}\text{-}r\text{-}Sar_{0.73})_{75}$	6.3	9.3	1.10
19	3:3	68%	$P(L\text{-}Leu_{0.4}\text{-}r\text{-}Sar_{0.6})_{90}$	8.1	8.3	1.20
20	4:2	65%	$P(L\text{-}Leu_{0.62}\text{-}r\text{-}Sar_{0.38})_{56}$	5.6	6.1	1.29
21	5:1	36%	$P(L\text{-}Leu_{0.82}\text{-}r\text{-}Sar_{0.18})_{72}$	7.1	5.1	1.53

[a] Conditions: monomer (2.0 mmol overall), DMSO (3 mL), 60 °C for 48 h.

[b] [AA-NPC]:[BzA] = 100:1, [Sar-NPC]:[DiPEA] = 100:16.

Table S4. The solubilities of polysarcosine, P(L-Phe-*r*-Sar) copolymers (Sample **1**, **3** and **5**) and poly(L-Phe) in various solvents at the concentration of 5 mg/mL (+: soluble, ○: partly soluble, -: insoluble).

Sample	H_2O	HFIP	DMF	CH_2Cl_2	THF
PSar	+	+	+	+	−
Sample **1** $P(L\text{-}Phe_{0.08}\text{-}r\text{-}Sar_{0.92})_{73}$	+	+	+	−	−
Sample **3** $P(L\text{-}Phe_{0.38}\text{-}r\text{-}Sar_{0.62})_{52}$	−	−	+	−	−
Sample **5** $P(L\text{-}Phe_{0.79}\text{-}r\text{-}Sar_{0.21})_{56}$	−	−	−	○	−
PPhe	−	−	−	−	−

Table S5. Solubilities of polysarcosine, P(BLL-*r*-Sar) copolymers (Sample **7**, **9**, **11)** and polyBLL in different solvents at the concentration of 5 mg/mL (+: soluble, ○: partly soluble, -: insoluble).

Sample	H_2O HFIP DMF CH_2Cl_2 THF
PSar	
Sample **7** $P(BLL_{0.1}$-*r*-$Sar_{0.9})_{100}$	
Sample **9** $P(BLL_{0.47}$-*r*-$Sar_{0.53})_{77}$	
Sample **11** $P(BLL_{0.88}$-*r*-$Sar_{0.12})_{142}$	
PBLL	

Table S6. Solubilities of polysarcosine, P(L-Leu-*r*-Sar) copolymers (Sample **17**, **19**, **21)** and polyleucine in different solvents at the concentration of 5 mg/mL (+: soluble, ○: partly soluble, -: insoluble).

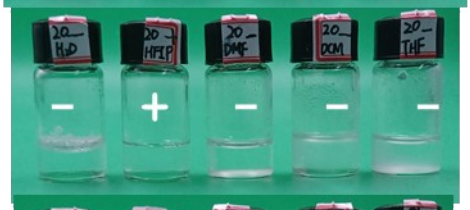
Sample	H_2O HFIP DMF CH_2Cl_2 THF
PSar	
Sample **17** P(L-Leu$_{0.1}$-*r*-Sar$_{0.9}$)$_{110}$	
Sample **19** P(L-Leu$_{0.4}$-*r*-Sar$_{0.6}$)$_{90}$	
Sample **21** P(L-Leu$_{0.82}$-*r*-Sar$_{0.18}$)$_{72}$	
PLeu	

Table S7. Nanoparticles produced from Sample **13** and **14**, the copolymer of OBLS and sarcosine.

Sample	Polymer composition by NMR	Number Mean Diameter [a] (nm)	Intensity Mean Diameter [a] (nm)	PDI [a]
13	$P(OBLS_{0.1}\text{-}r\text{-}Sar_{0.9})_{78}$	68	131	0.128
14	$P(OBLS_{0.24}\text{-}r\text{-}Sar_{0.76})_{83}$	76	123	0.103

[a] Estimated from DLS characterization.

Table S8. Nanoparticle s produced from Sample **9-11**, the copolymer of BLL and sarcosine.

Sample	Polymer composition by NMR	Number Mean Diameter [a] (nm)	Intensity Mean Diameter [a] (nm)	PDI [a]
9	$P(BLL_{0.47}\text{-}r\text{-}Sar_{0.53})_{77}$	35	59	0.187
10	$P(BLL_{0.63}\text{-}r\text{-}Sar_{0.37})_{76}$	33	121	0.173
11	$P(BLL_{0.8}\text{-}r\text{-}Sar_{0.128})_{142}$	19	39	0.183

[a] Estimated from DLS characterization.

Equations S1-S3. Calculation of the molar ratio of AA-NPCs, AA-NCAs and residues from *in situ* NMR spectra.

$$\frac{[AA-NPC]_t}{[AA-NPC]_0} = \frac{I_{AA-NPC_t}}{I_{AA-NPC_0}} \quad \text{(S1)}$$

$$\frac{[AA-NCA]_t}{[AA-NPC]_0} = \frac{I_{AA-NCA_t}}{I_{AA-NPC_0}} \quad \text{(S2)}$$

$$\frac{[residue]_t}{[AA-NPC]_0} = \frac{I_{residue_t}}{I_{AA-NPC_0}} \quad \text{(S3)}$$

I_{AA-NPC_0} means integral of proton of AA-NPC linking C_α before heating.

I_{AA-NPC_t} means integral of proton of AA-NPC linking C_α after heating for *t* hours.

I_{AA-NCA_t} means integral of proton of AA-NCA linking C_α after heating for *t* hours

$I_{residue_t}$ means integral of proton linking C_α of corresponding amino acid residue after heating for *t* hours

Equation S4. First order kinetics of AA-NPC polymerization.

$$\ln\frac{[AA-NPC]_0}{[AA-NPC]_t} = k_d t$$

Here, the decomposition of AA-NPC is treated as a first order kinetics reaction.

$[AA-NPC]_t$ means concentration of AA-NPC at time *t*.

$[AA-NPC]_0$ means concentration of AA-NPC in feed.

k_d means the consumption reaction rate constant of AA-NPC.

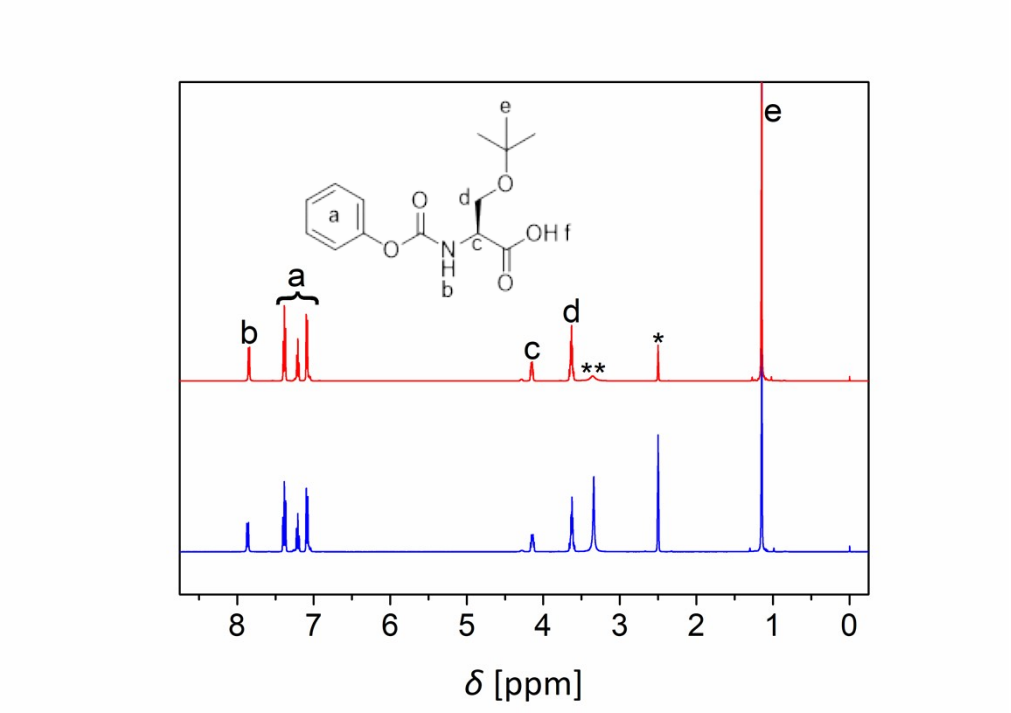
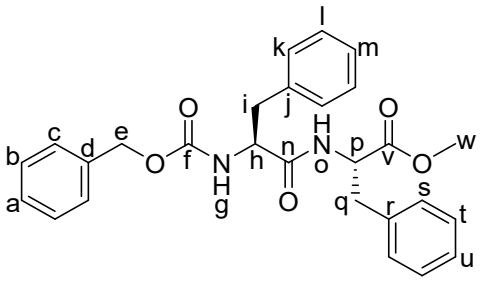


Fig. S1. ^{1}H NMR spectra of the same OBLS-NPC sample on May 21, 2019 (blue) and September 7, 2021 (red) stored under ambient condition (* DMSO, ** H_2O).

A



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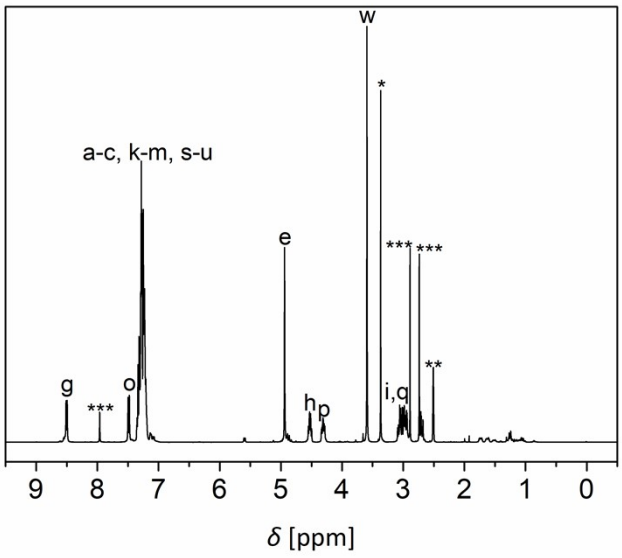

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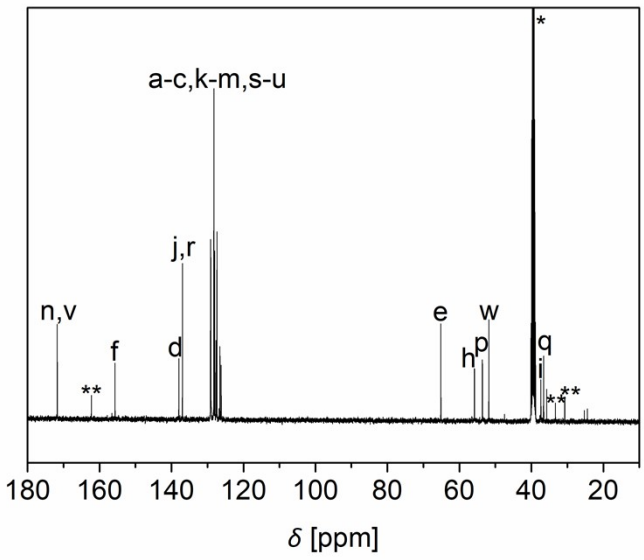
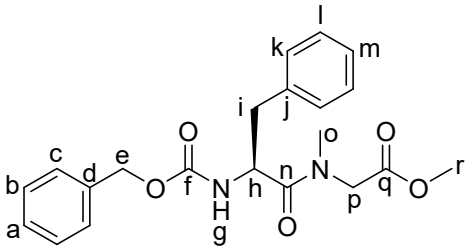


Fig. S2. (A) Phe-Phe dipeptide (methyl *N*-(benzyloxycarbonyl-L-phenylalanyl)-L-phenylalaninate). (B) ^{1}H NMR spectrum of Phe-Phe dipeptide (* H_2O, ** DMSO, ***DMF). (C) ^{13}C NMR spectrum of Phe-Phe dipeptide (* DMSO, **DMF).

A



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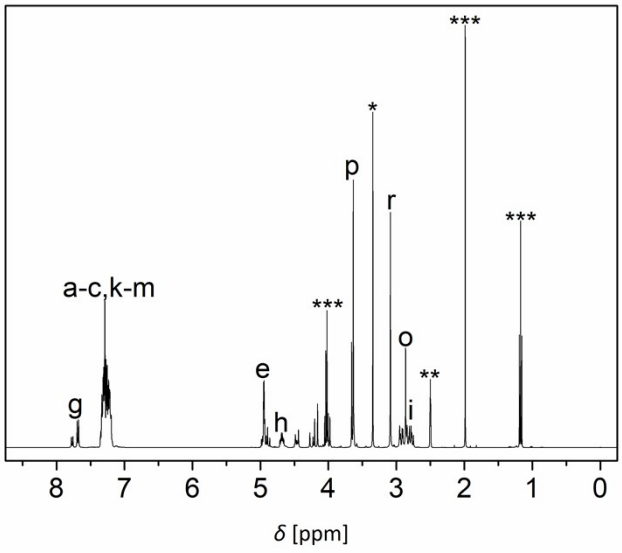

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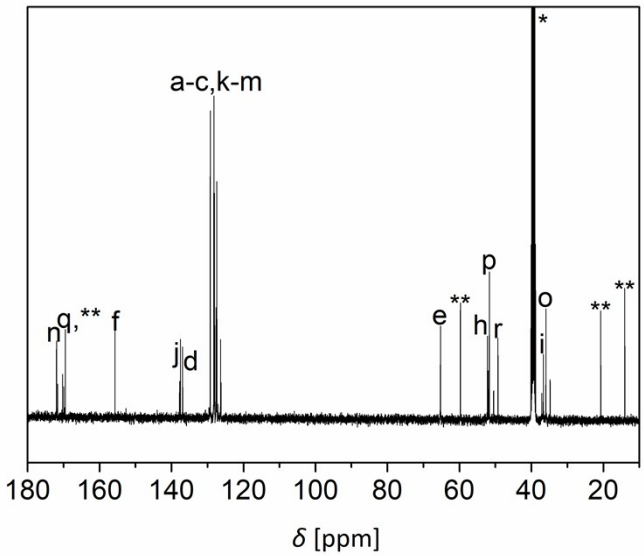
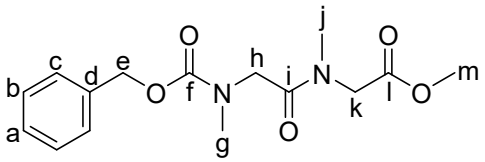


Fig. S3 (A) Phe-Sar dipeptide (methyl *N*-(benzyloxycarbonyl-L-phenylalanyl)-sarcosinate). (B) ^{1}H NMR spectrum of Phe-Sar dipeptide (* H_2O, ** DMSO, ***EA). (C) ^{13}C NMR spectrum of Phe-Sar dipeptide (* DMSO, **EA).

A



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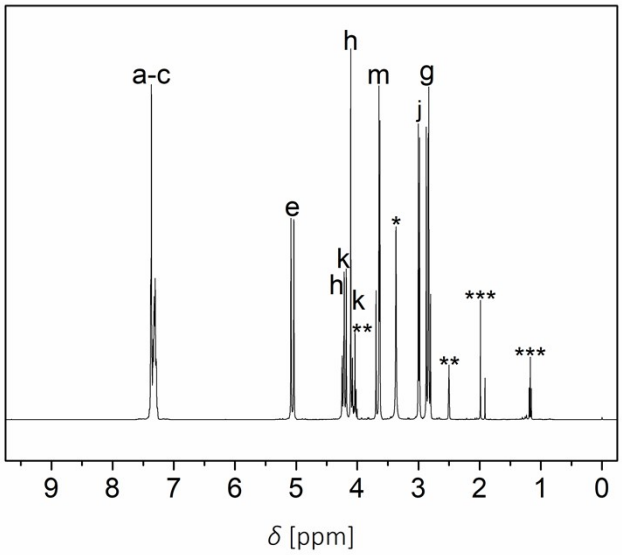

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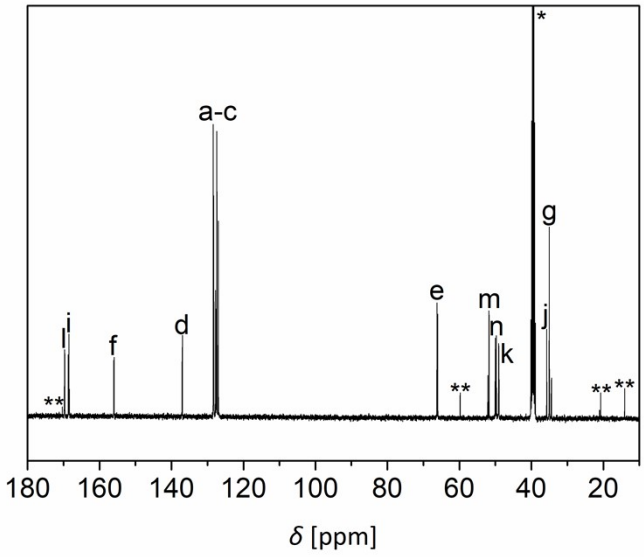
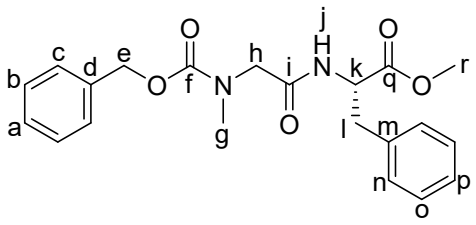


Fig. S4. (A) Sar-Sar dipeptide (methyl *N*-(benzyloxycarbonyl-sarcosinyl)-sarcosinate). (B) ^{1}H NMR spectrum of Sar-Sar dipeptide (* H_2O, ** DMSO, ***EA). (C) ^{13}C NMR spectrum of Sar-Sar dipeptide (* DMSO, **EA).

A



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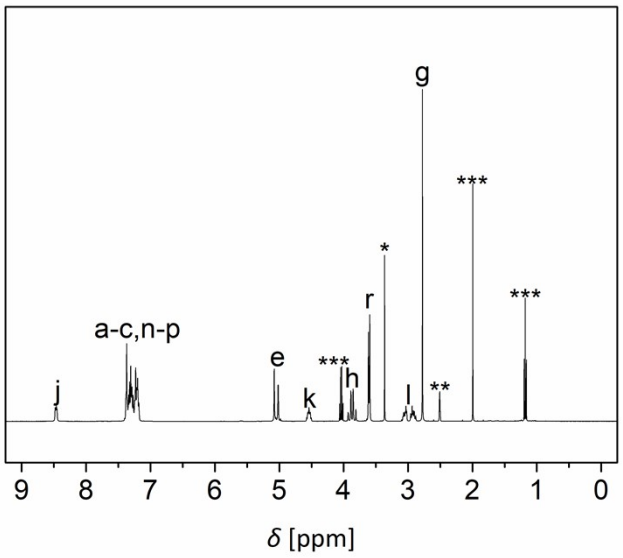


C

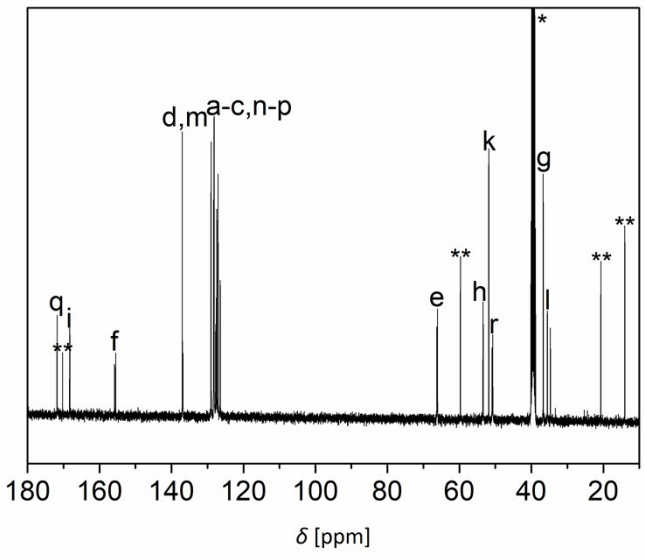


Fig. S5. (A) Sar-Phe dipeptide (methyl *N*-(benzyloxycarbonyl-sarcosinyl)-L-phenylalanate). (B) ^{1}H NMR spectrum of Sar-Phe dipeptide (* H_2O, ** DMSO, ***EA). (C) ^{13}C NMR spectrum of Sar-Phe dipeptide (* DMSO, **EA).

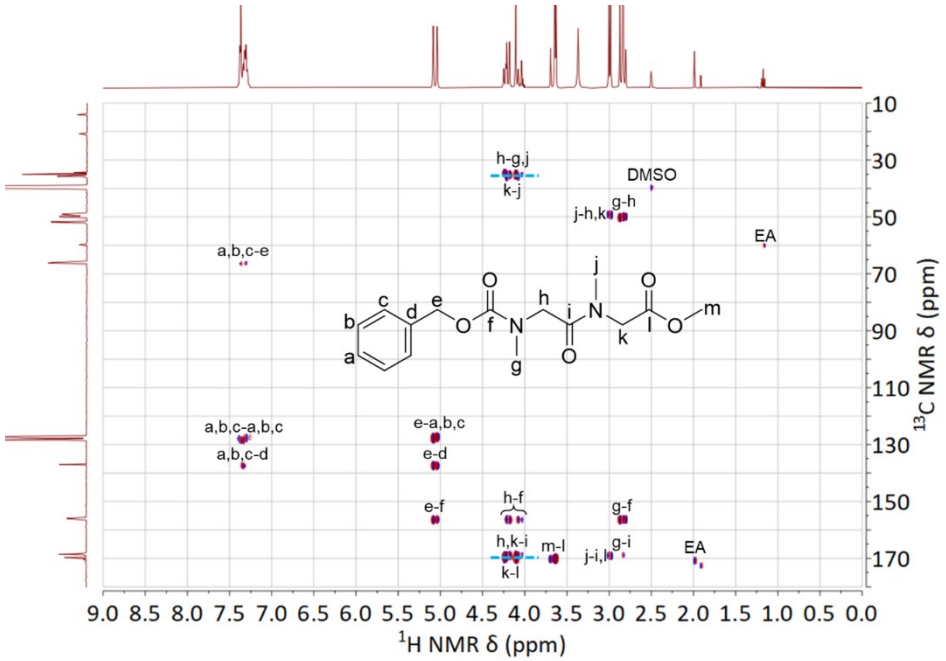


Fig. S6. HMBC NMR spectrum of Sar-Sar dipeptide (methyl *N*-(benzyloxycarbonyl-sarcosinyl)-sarcosinate) (letter before the hyphen notes the proton attaching the carbon, and the other after the hyphen notes the carbon atom).

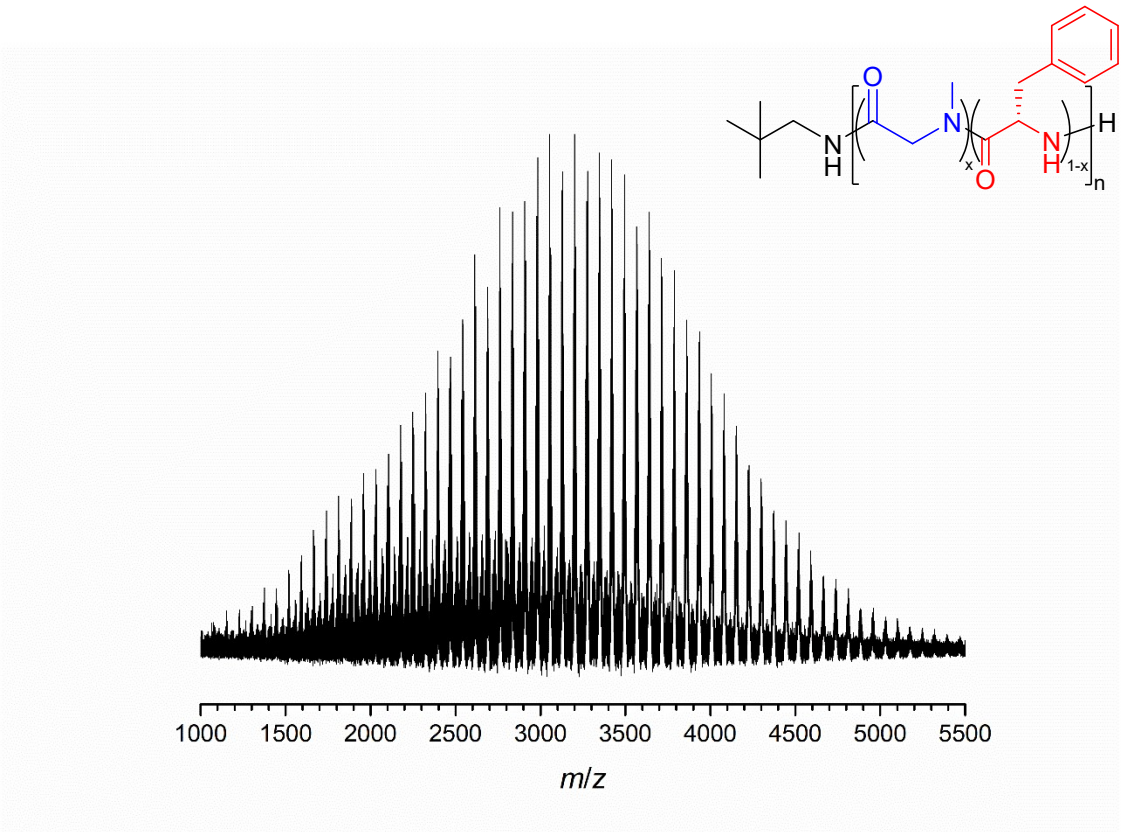


Fig. S7. MALDI-ToF MS of Sample **6**.

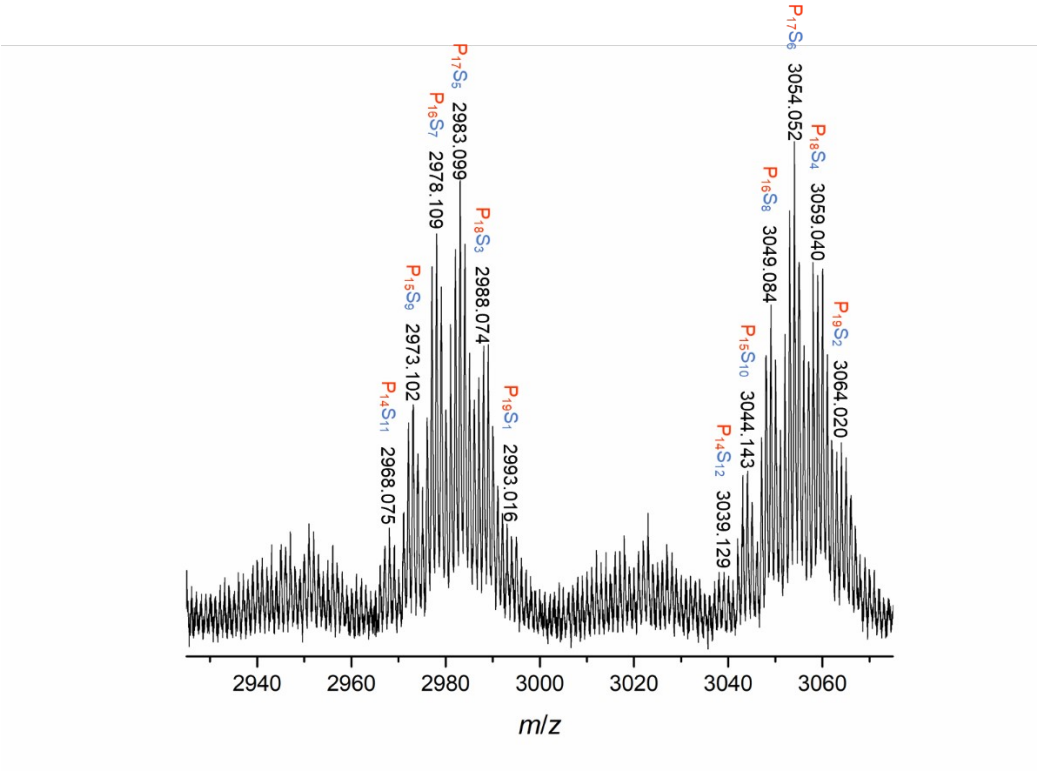


Fig. S8. Enlarged MALDI-ToF MS of Sample **6** between m/z=2930-3070 (K^+ as counter-ion, P: phenylalanine residue, S: sarcosine residue, neopentylamine as initiator).

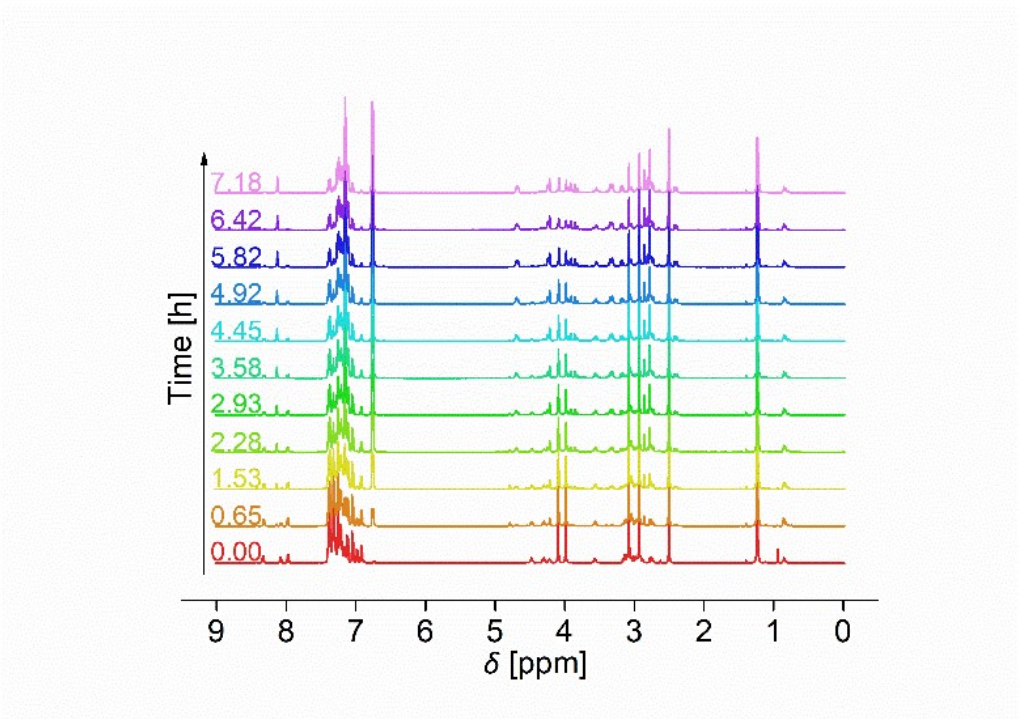


Fig. S9. Copolymerization of L-Phe-NPC with Sar-NPC monitored by ^{1}H NMR spectra.

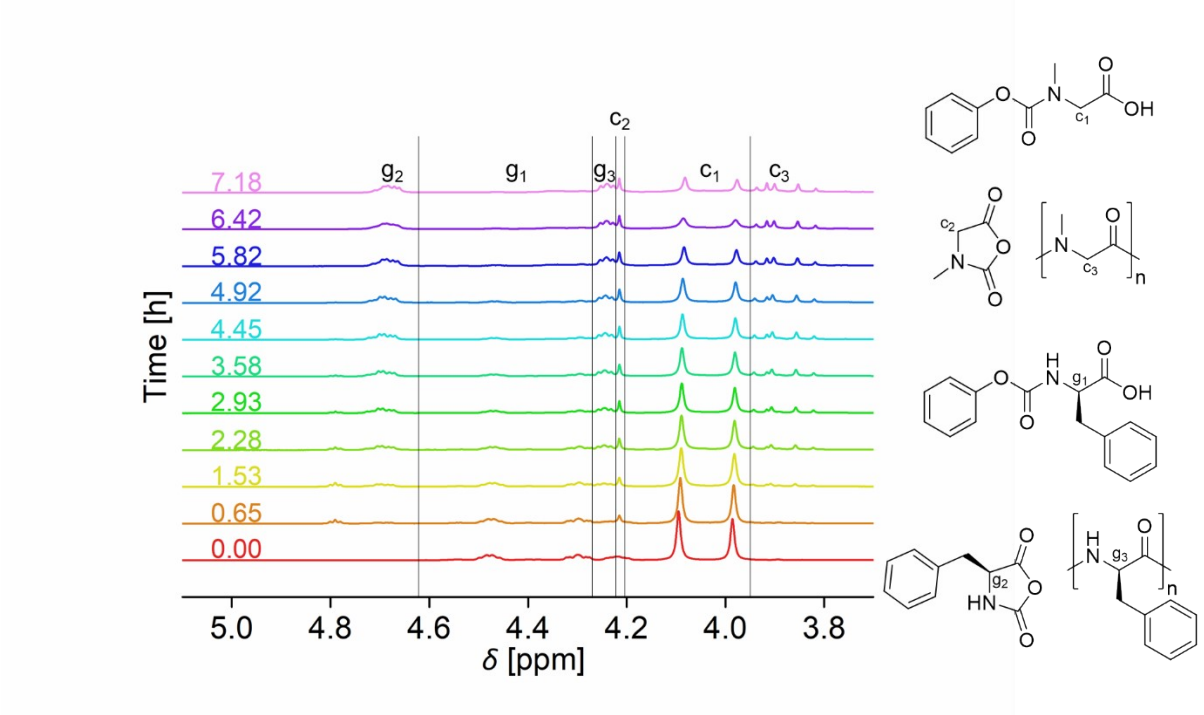


Fig. S10. Enlarged ^{1}H NMR spectra between δ = 3.7-5.1 ppm during copolymerization of L-Phe-NPC with Sar-NPC.

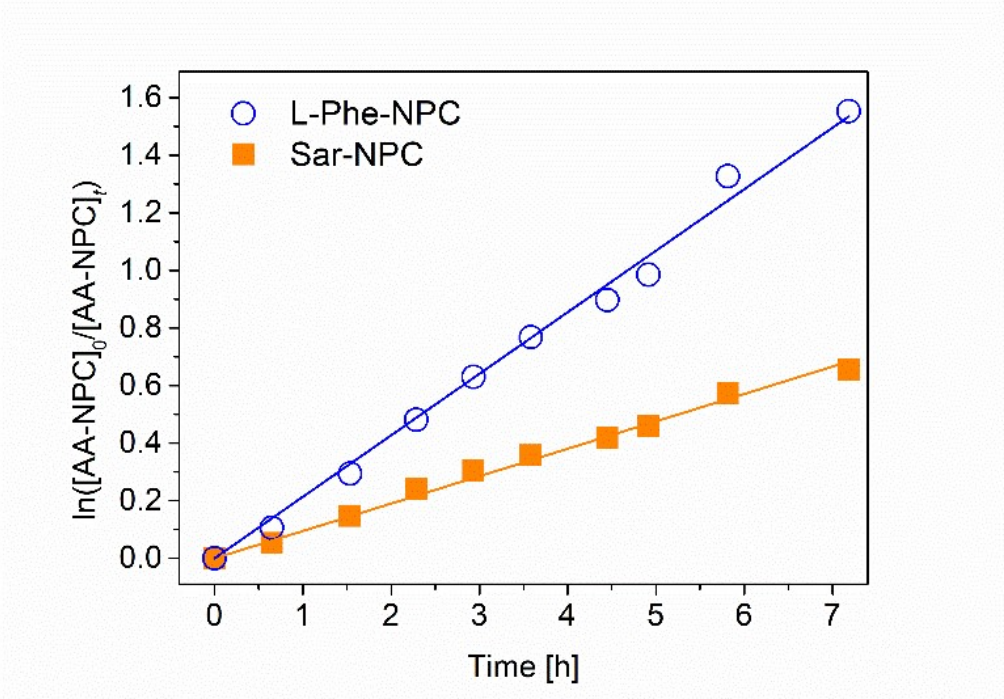


Fig. S11. Plot of pseudo-first-order kinetics derived from the ^{1}H NMR analysis.

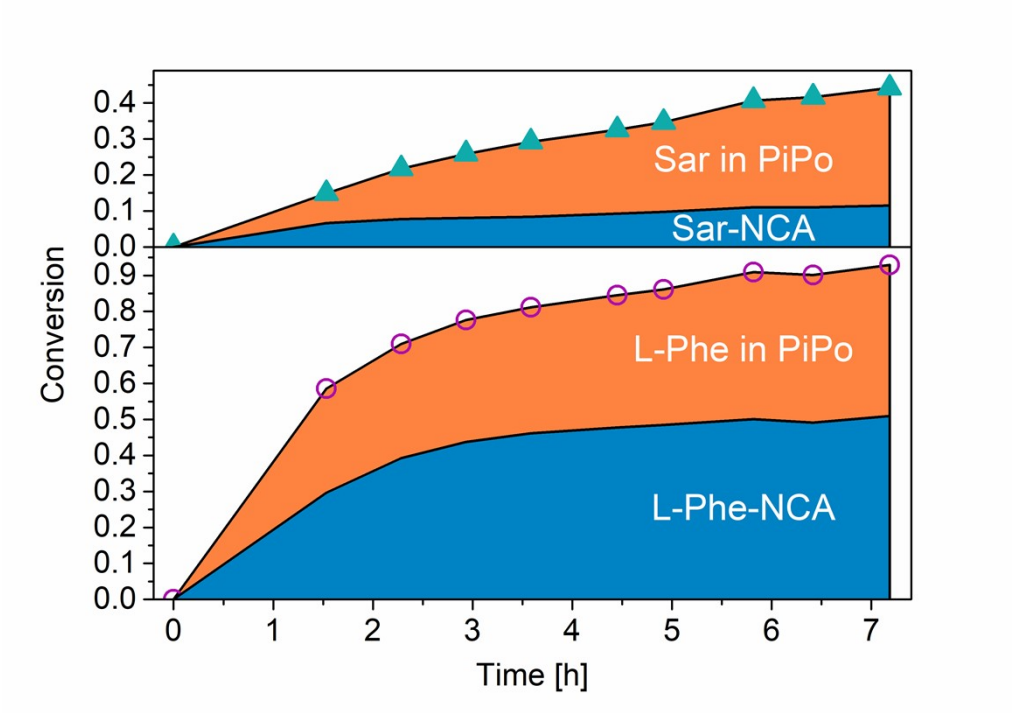


Fig. S12. Conversion of sarcosine and phenylalanine-related species during copolymerization.

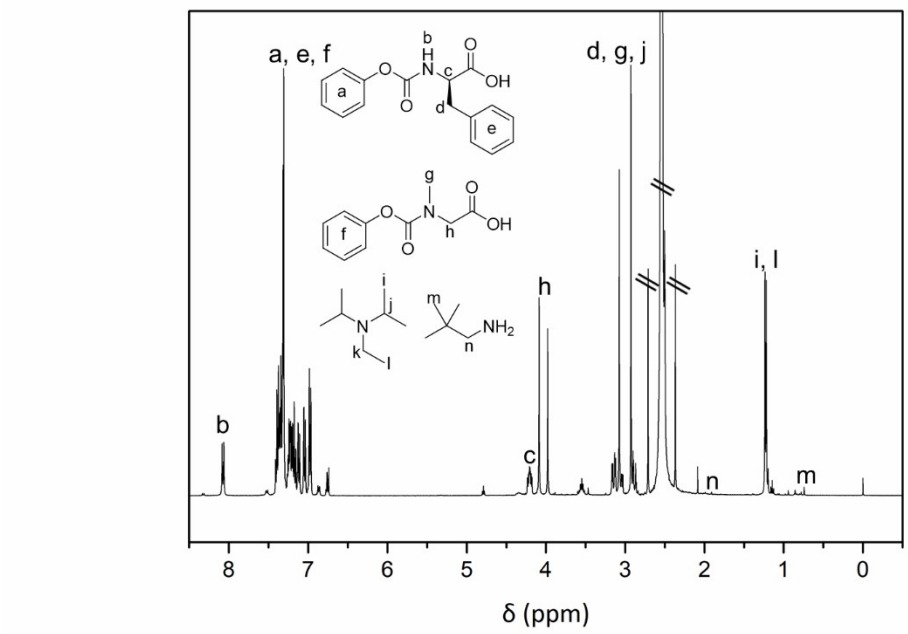


Fig. S13. ^{1}H NMR spectrum of the reaction mixture of L-Phe-NPC, Sar-NPC, neopentylamine and diisopropylethylamine after 48 h at room temperature (=: DMSO).

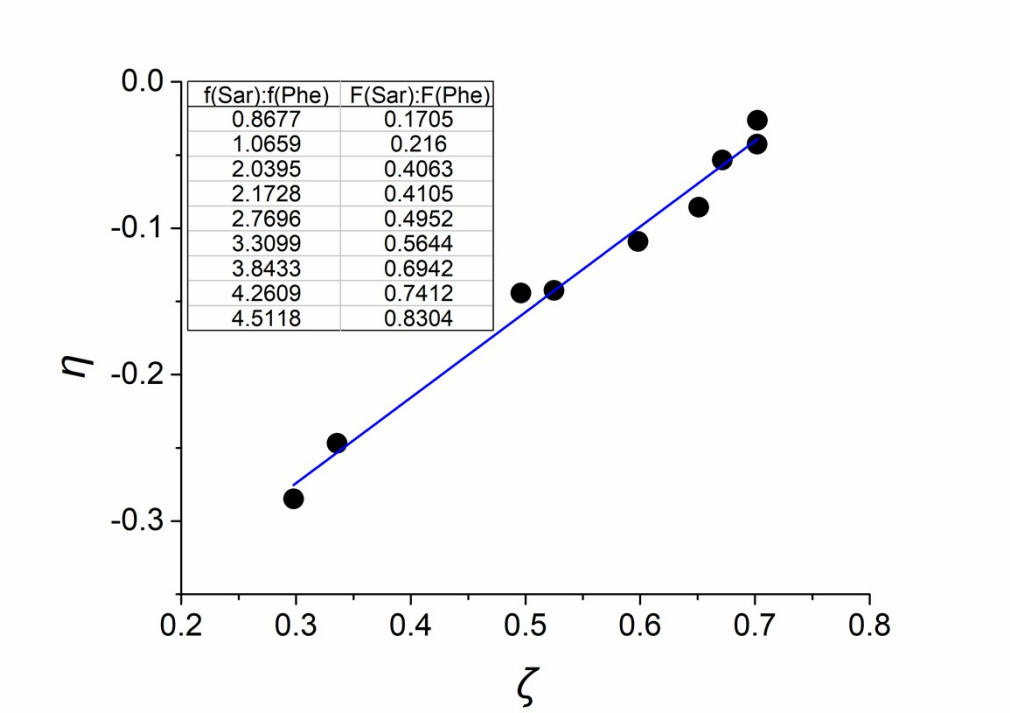
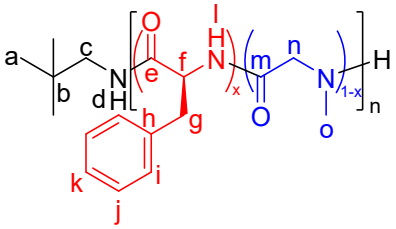
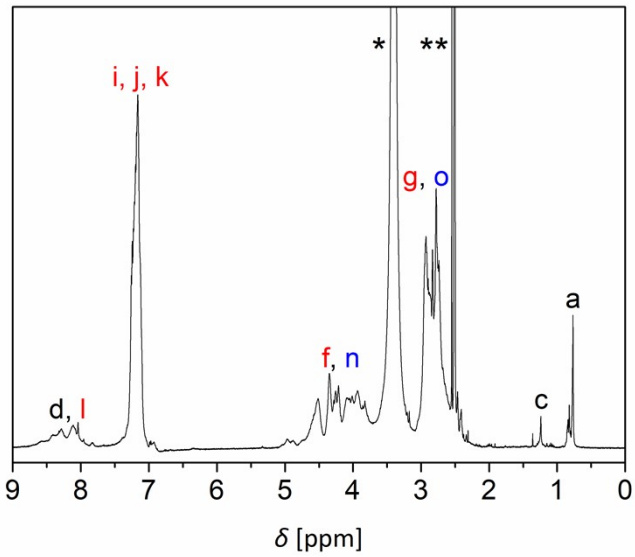


Fig. S14. η-ζ diagram for Kelen-Tüdos method of Sar-NPC/L-Phe-NPC copolymerization (r^2 = 0.9839, $r_{\text{L-Phe-NPC}}$ = 4.675, $r_{\text{Sar-NPC}}$ = 0.135).

A



B



C

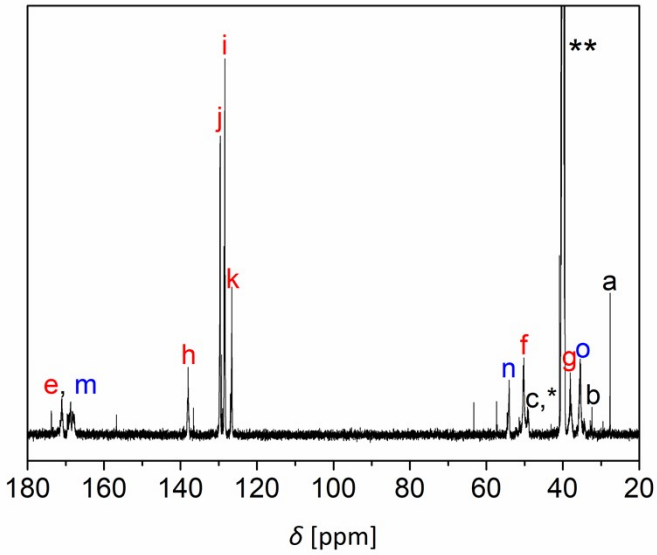
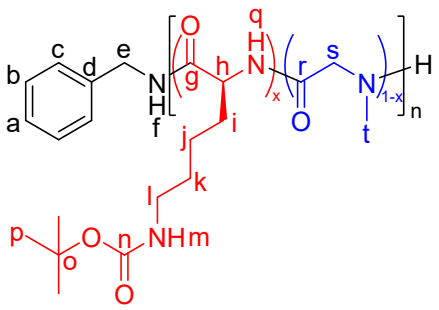
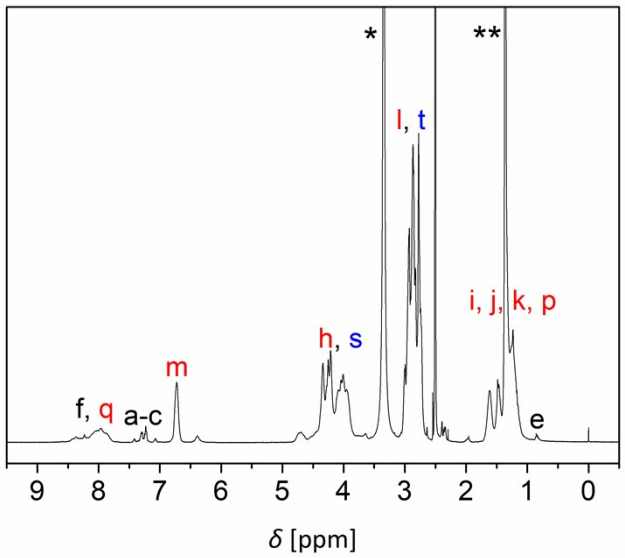


Fig. S15. (A) P(L-Phe$_{0.38}$-*r*-Sar$_{0.62}$)$_{52}$ (Sample **3** in Table 1). (B) ^{1}H NMR spectrum of Sample **3** (* H_2O, ** DMSO). (C) ^{13}C NMR spectrum of Sample **3** (* methanol, ** DMSO).

A



B



C

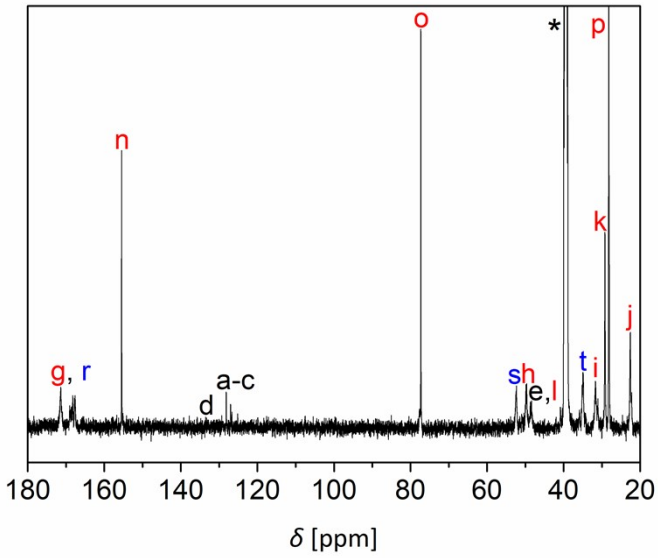


Fig. S16. (A) P(BLL$_{0.47}$-*r*-Sar$_{0.53}$)$_{77}$ (Sample **9** in Table S1). (B) ^{1}H NMR spectrum of Sample **9** (* H_2O, ** DMSO). (C) ^{13}C NMR spectrum of Sample **9** (* DMSO).

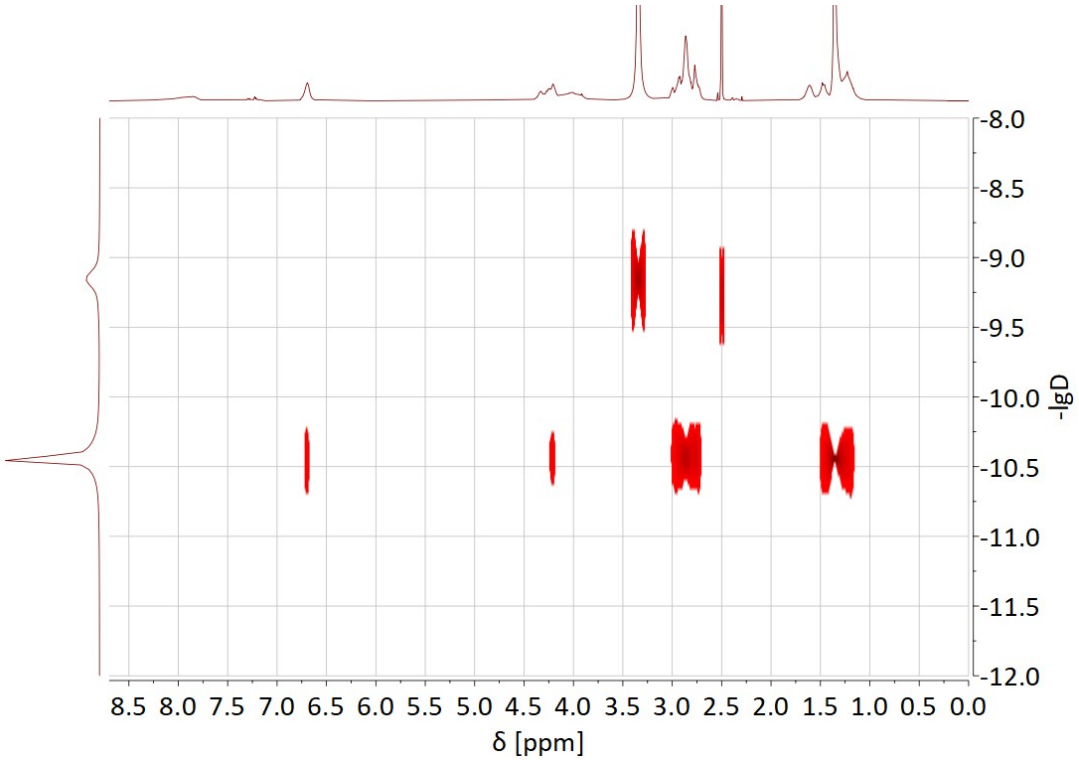


Fig. S17. DOSY NMR spectrum of Sample **9**.

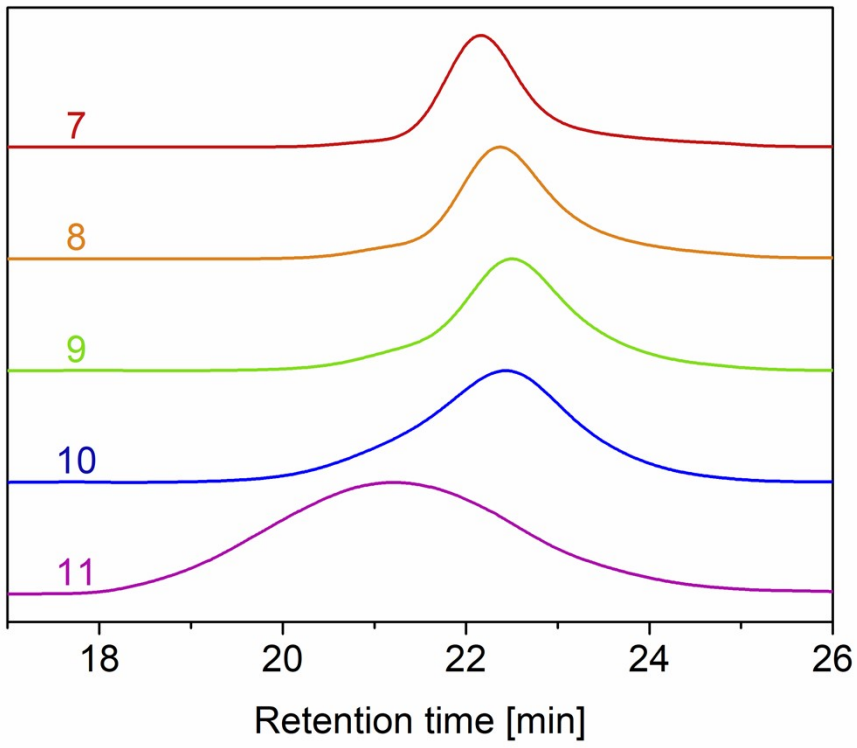
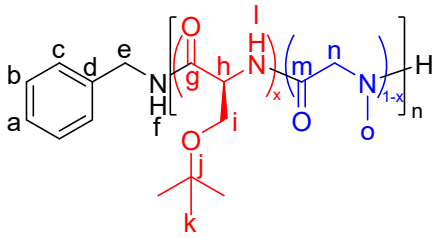
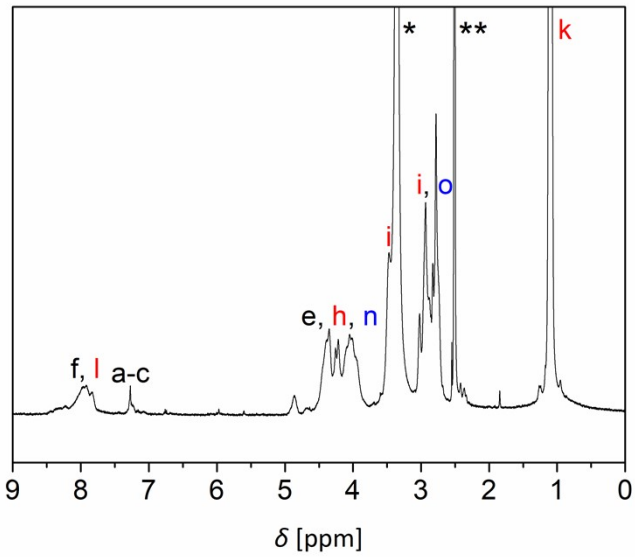


Fig. S18. SEC traces of Sample **7**-**11**.

A



B



C

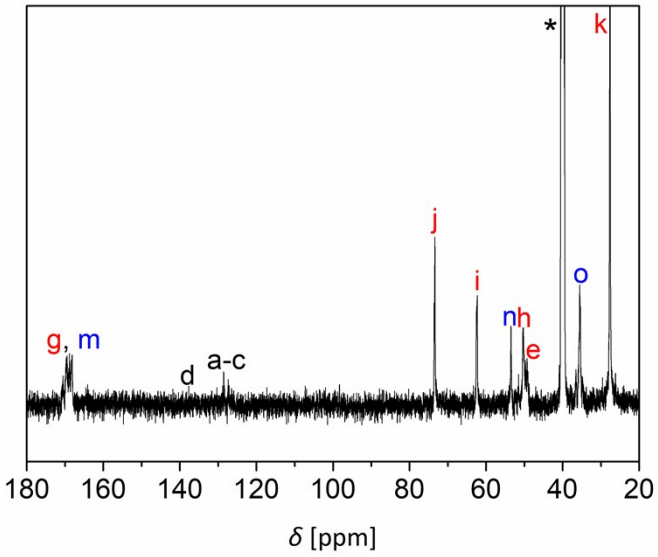


Fig. S19. (A) P(OBLS$_{0.47}$-*r*-Sar$_{0.53}$)$_{99}$ (Sample **14** in Table S2). (B) ^{1}H NMR spectrum of Sample **14** (* H_2O, ** DMSO). (C) ^{13}C NMR spectrum of Sample **14** (* DMSO).

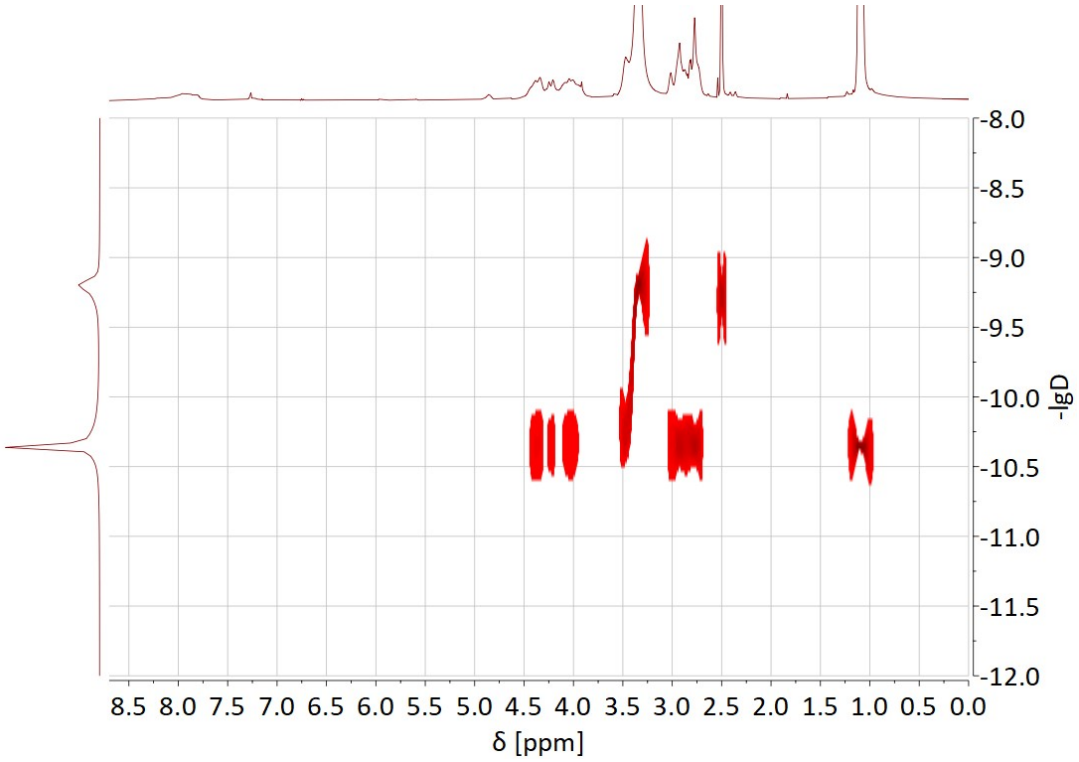


Fig. S20. DOSY NMR spectrum of Sample **14**.

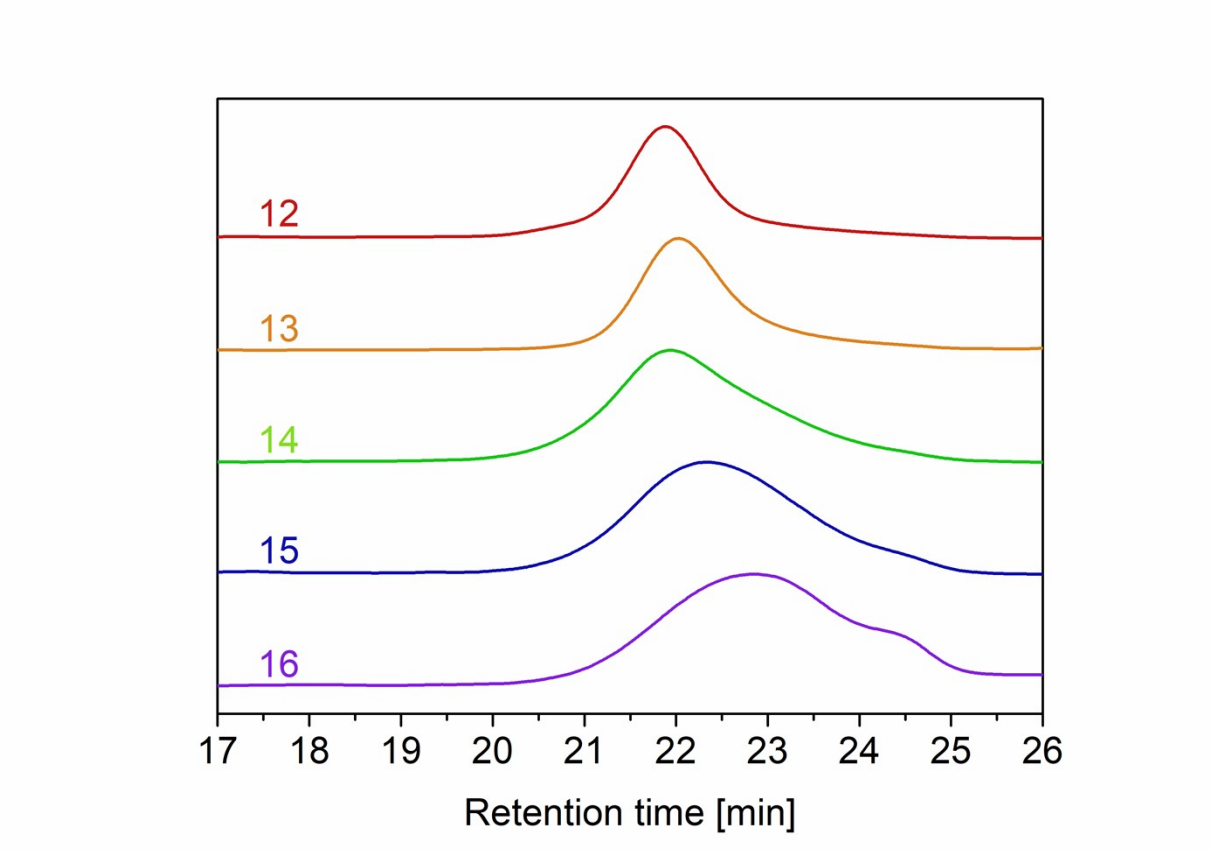
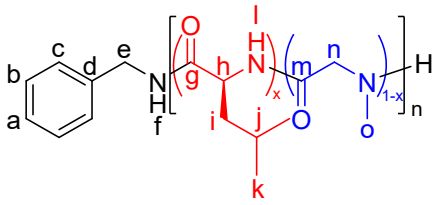
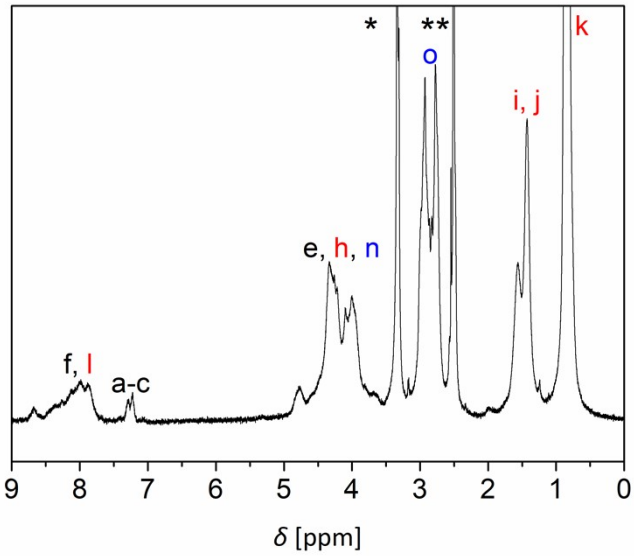


Fig. S21. SEC traces of Sample **12-16**.

A



B



C

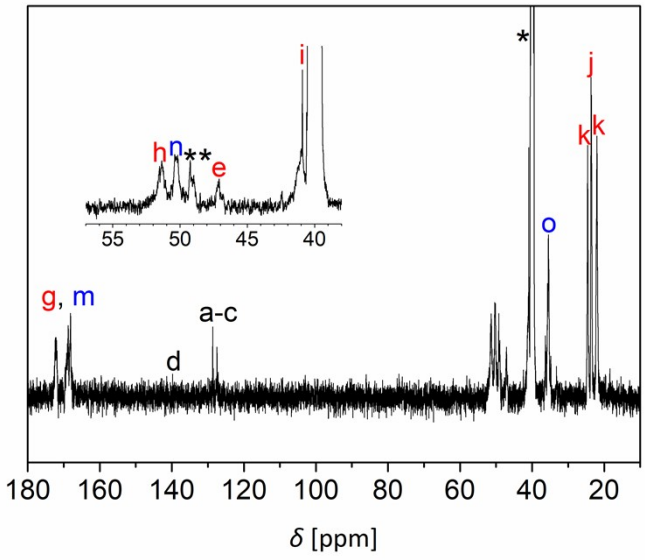


Fig. S22. (A) P(L-Leu$_{0.4}$-*r*-Sar$_{0.6}$)$_{90}$ (Sample **19** in Table S3). (B) ^{1}H NMR spectrum of Sample **19** (* H_2O, ** DMSO). (C) ^{13}C NMR spectrum of Sample **19** (* DMSO).

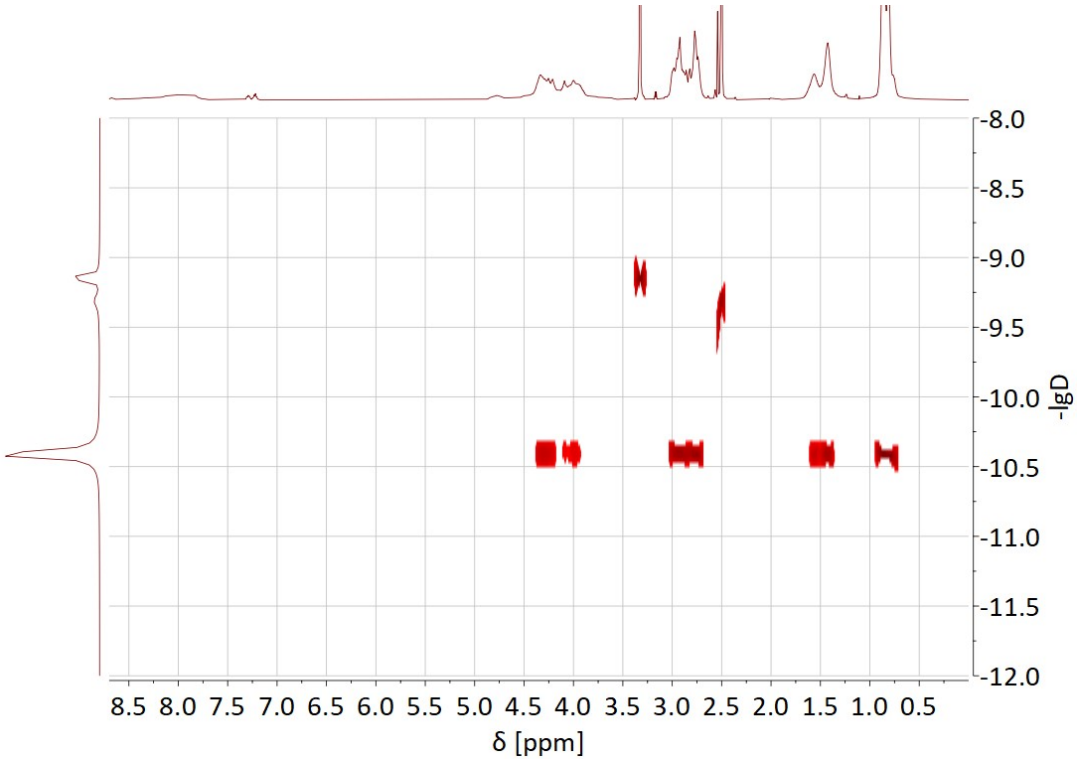


Fig. S23. DOSY NMR spectrum of Sample **19**.

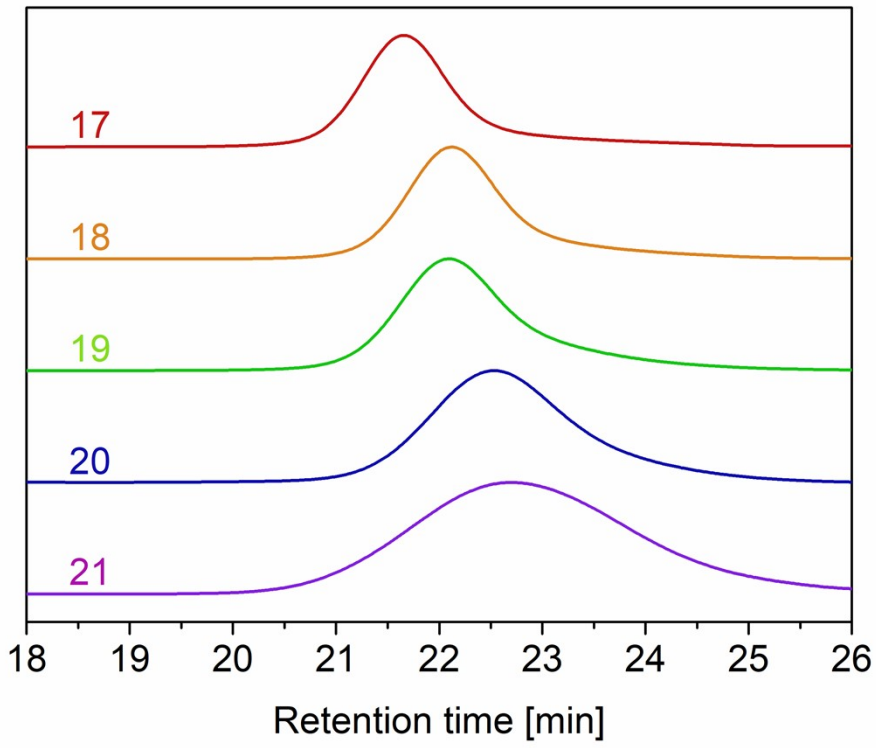


Fig. S24. SEC traces of Sample **17**-**21**.

Table S9 Integrals of the ^{1}H NMR at supporting information

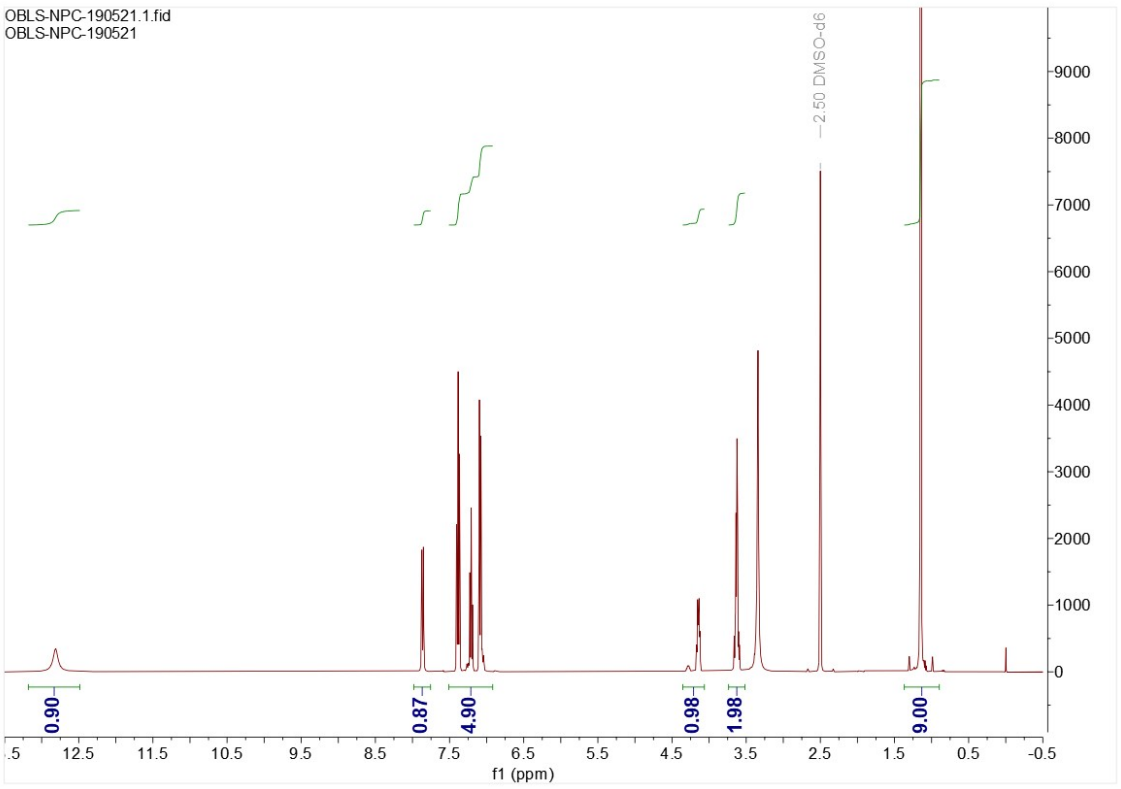
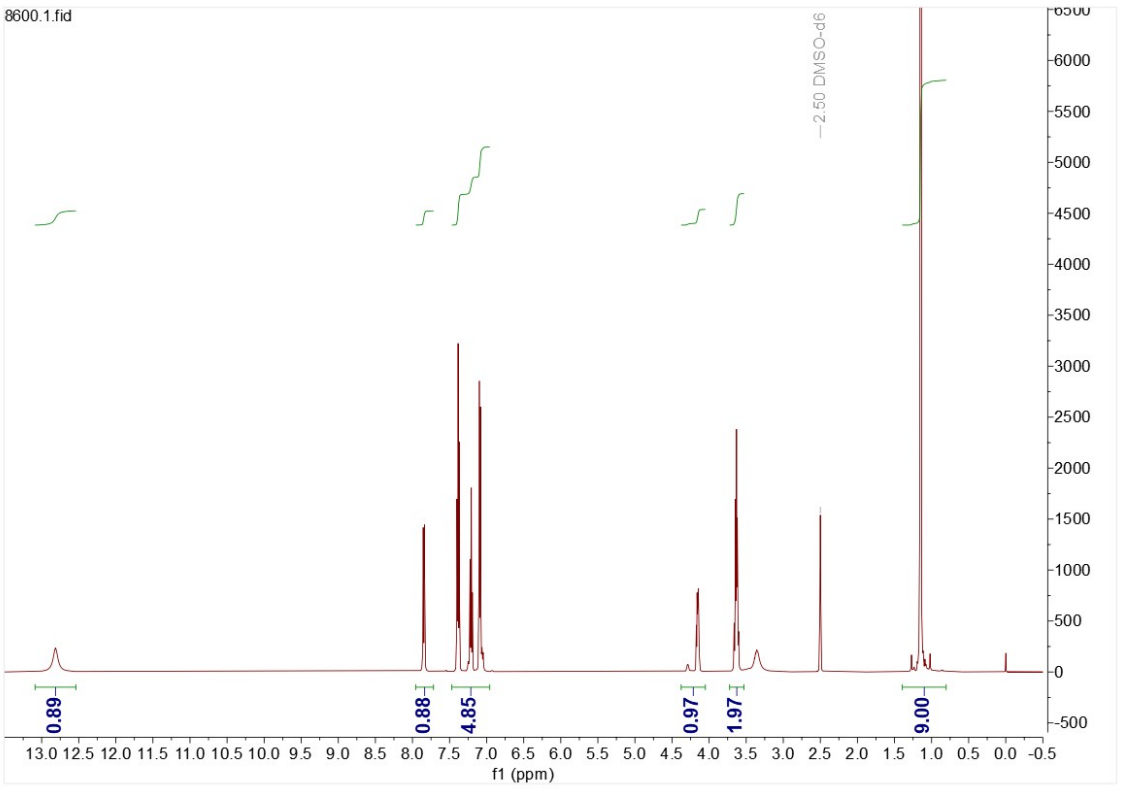
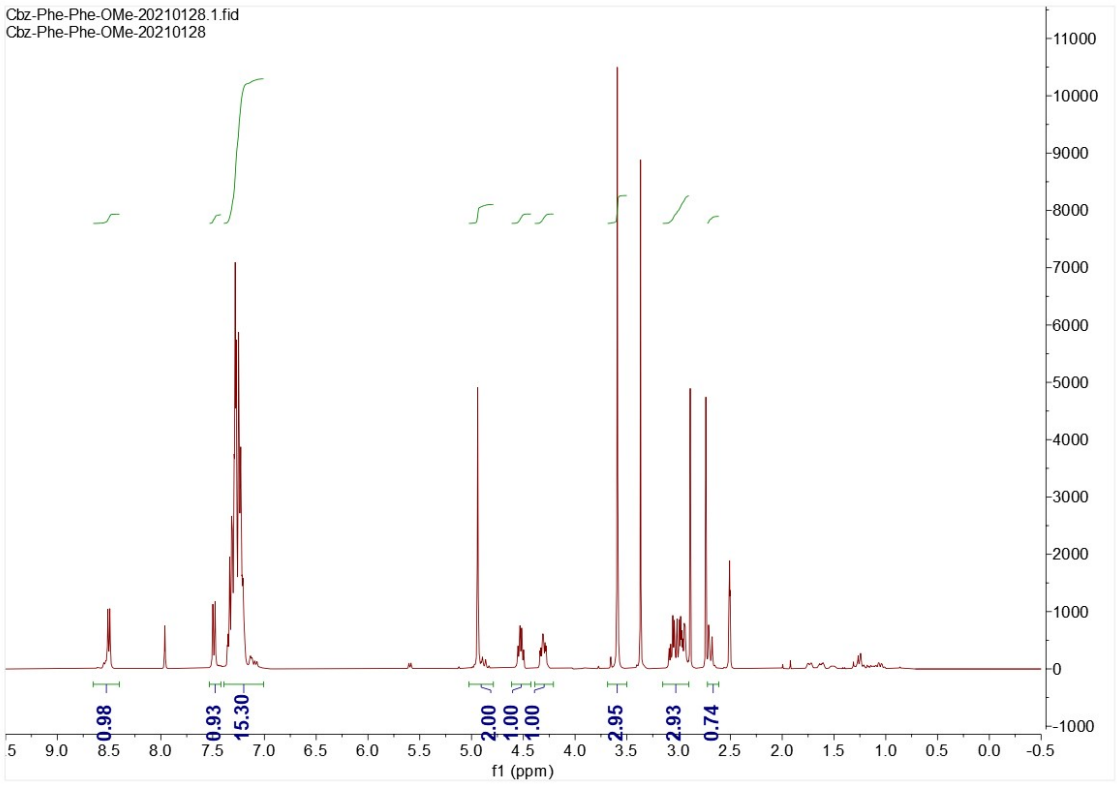
Original Figure	Integrals
Fig. S1 red	
Fig. S1 blue	
Fig. S2B	

Table S9 (Continued)

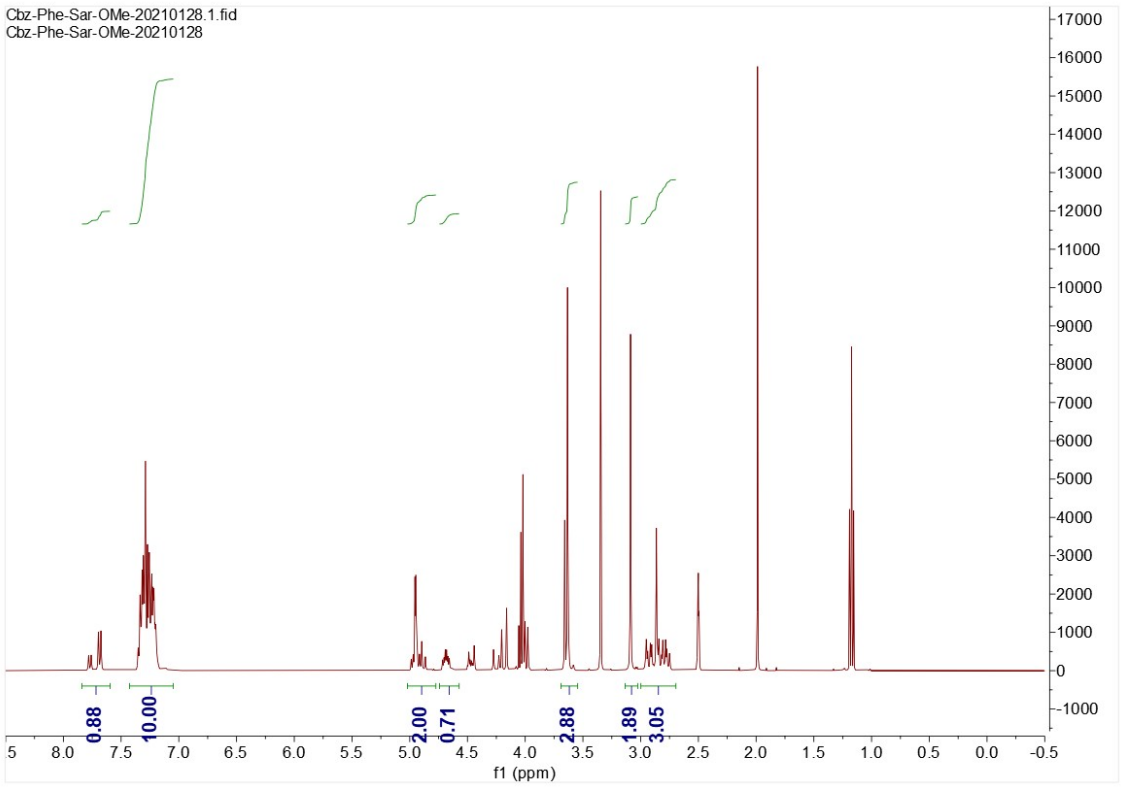
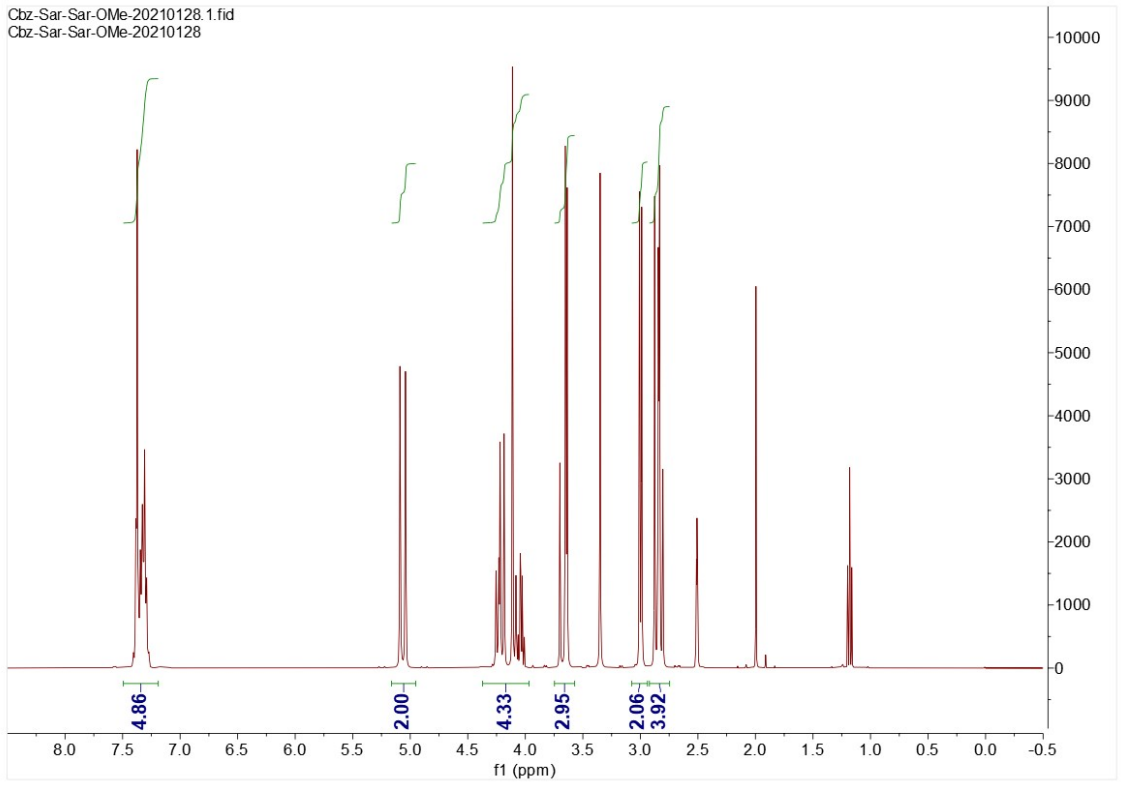
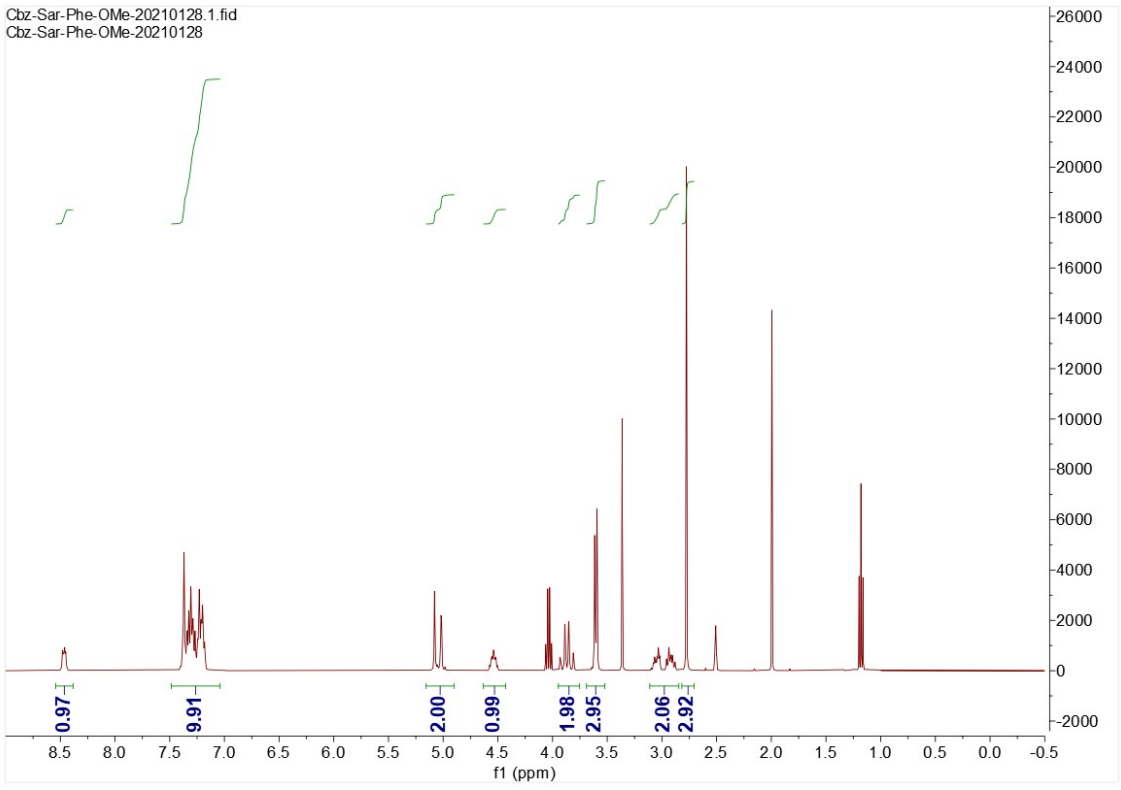
Original Figure	Integrals
Fig. S3B	
Fig. S4B	
Fig. S5B	

Table S9 (Continued)

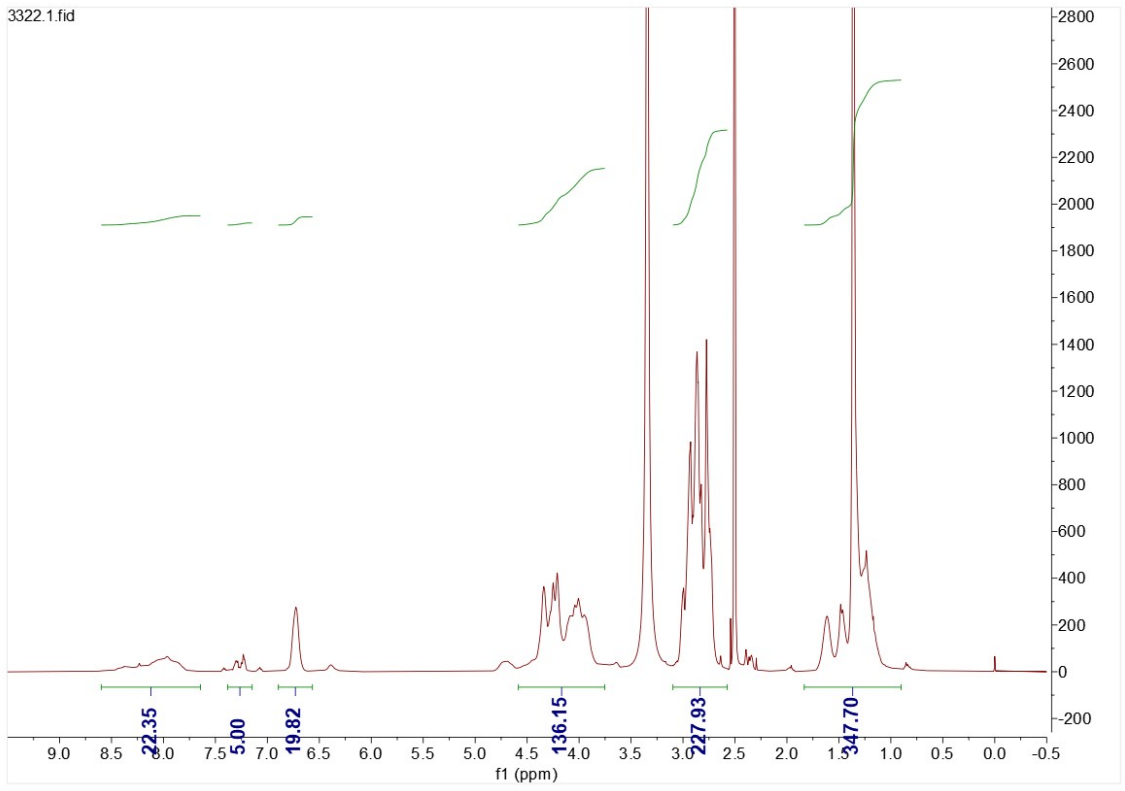
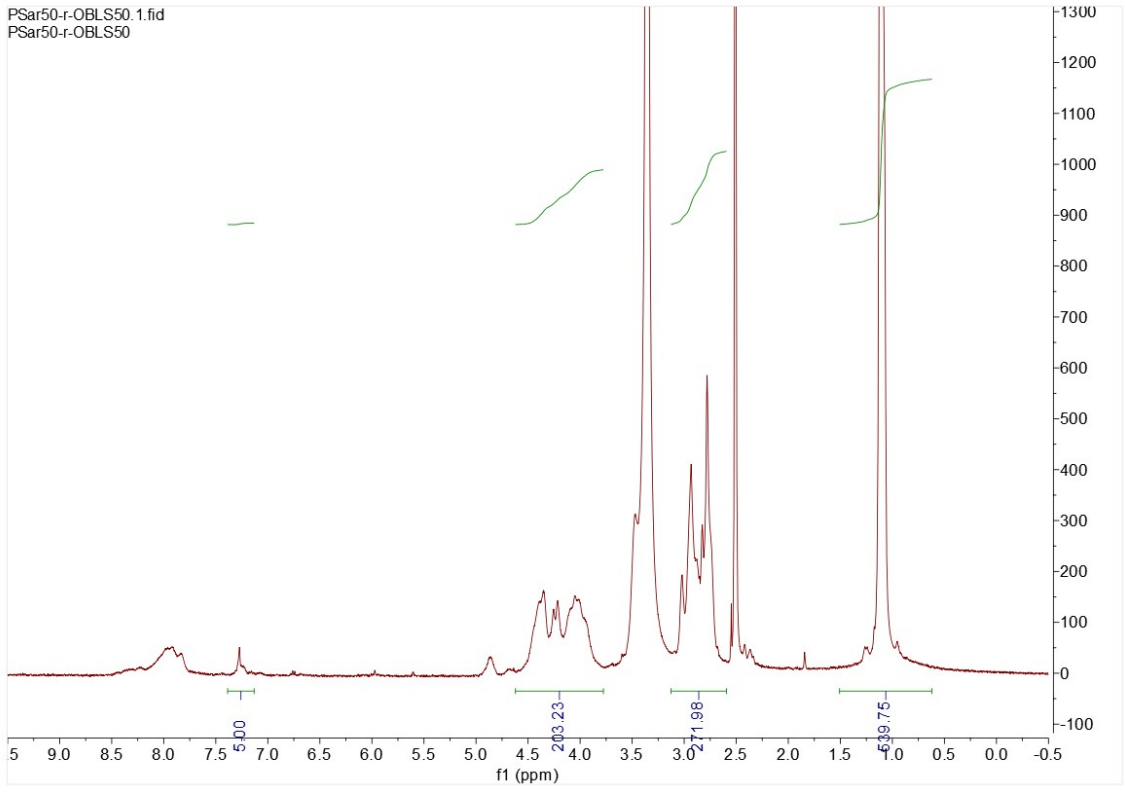
Original Figure	Integrals
Fig. S14B	
Fig. S15B	
Fig. S18B	

Table S9 (Continued)

Original Figure	Integrals
Fig. S21B	

Table SX Polymerization rate constants of AA-NCAs with various initiators in literatures. [a]

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	k_2 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	Notes
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10			23.11		Nitrogen pressure = 0.5 mbar
	sarcosine	benzonitrile	benzylamine	room temperature	0.5	10			305		Nitrogen pressure = 0.5 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10			19.87		Nitrogen pressure = 5 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10			20.93		Nitrogen pressure = 50 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10			28.78		Put in closed vessel
	N-ethylglycine	benzonitrile	benzylamine	room temperature	0.5	10			7.41		Nitrogen pressure = 5 mbar
	N-ethylglycine	benzonitrile	benzylamine	room temperature	0.5	10			2.34		Nitrogen pressure = 50 mbar
	N-ethylglycine	benzonitrile	benzylamine	room temperature	0.5	10			8.54		Put in closed vessel
2	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10	trifluoromethane sulfonic acid	0.005	21.51		Nitrogen pressure = 0.5 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10	trifluoromethane sulfonic acid	0.05	17.07		Nitrogen pressure = 0.5 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10	trifluoromethane sulfonic acid	0.125	7.9		Nitrogen pressure = 0.5 mbar
	sarcosine	*N*-methyl-2-pyrrolidinone	benzylamine	room temperature	0.5	10	trifluoromethane sulfonic acid	0.25	2.36		Nitrogen pressure = 0.5 mbar
	N-ethylglycine	benzonitrile	benzylamine	room temperature	1	40			6.28		Nitrogen pressure = 40 mbar
	N-ethylglycine	benzonitrile	benzylamine	room temperature	1	20			6.3		Nitrogen pressure = 40 mbar
	N-*n*-propylglycine	benzonitrile	benzylamine	room temperature	1	40			4.6		Nitrogen pressure = 40 mbar
	N-*n*-propylglycine	benzonitrile	benzylamine	room temperature	1	20			5.5		Nitrogen pressure = 40 mbar
	N-*n*-butylglycine	benzonitrile	benzylamine	room temperature	1	40			4.08		Nitrogen pressure = 40 mbar
	N-*n*-butylglycine	benzonitrile	benzylamine	room temperature	1	20			4.46		Nitrogen pressure = 40 mbar
	N-isobutyl-glycine	benzonitrile	benzylamine	room temperature	1	40			2.71		Nitrogen pressure = 40 mbar

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
3	γ-benzyl L-glutamate	dimethylformamide	diethylamine	25 °C	0.25	3.5			216.67		
	γ-benzyl L-glutamate	dimethylformamide	diethylamine	25 °C	0.05	3.5			175		
	γ-benzyl L-glutamate	dimethylformamide	diethylamine	25 °C	0.02	3.5			141.67		
	N_6-*tert*-butoxycarbonyl-L-lysine	dimethylformamide	diethylamine	25 °C	0.025	3.5			55		
	N_6-*tert*-butoxycarbonyl -L-lysine	dimethylformamide	diethylamine	25 °C	0.05	3.5			58.33		
	N_6-*tert*-butoxycarbonyl -L-lysine	dimethylformamide	diethylamine	25 °C	0.2	3.5			63.33		
4	sarcosine	benzene	*n*-hexylamine	25 °C	0.102	10			110	633.33	
	sarcosine	benzene	*n*-hexylamine	25 °C	0.1	5.3			130	566.67	
	sarcosine	benzene	*n*-hexylamine	25 °C	0.1	2.6			118.33	650	
5	glycine	dioxane	*n*-hexylamine	35 °C	- [e]	5			340		
	glycine	dioxane	*n*-hexylamine	35 °C	- [e]	0.5			400		
	N_6-*tert*-butoxycarbonyl -L-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	10			43.33		
	N_6-*tert*-butoxycarbonyl -L-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	5			40		
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	35 °C	- [e]	7.5			38.67		
	DL-alanine	dioxane	*n*-hexylamine	35 °C	- [e]	10			38.33		
	DL-alanine	dioxane	*n*-hexylamine	35 °C	- [e]	5			43.33		
	DL-alanine	dioxane	*n*-hexylamine	35 °C	- [e]	2.5			50		
	DL-2-aminobutanoic acid	dioxane	*n*-hexylamine	35 °C	- [e]	10			17.5		
	DL-2-aminobutanoic acid	dioxane	*n*-hexylamine	35 °C	- [e]	2.5			8		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
5	N_6-*tert*-butoxycarbonyl-DL-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	15			14.89		
	N_6-*tert*-butoxycarbonyl-DL-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	10			11.67		
	N_6-*tert*-butoxycarbonyl-DL-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	7.5			10.22		
	N_6-*tert*-butoxycarbonyl-DL-lysine	dioxane	*n*-hexylamine	35 °C	- [e]	5			8.33		
	DL-leucine	dioxane	*n*-hexylamine	35 °C	- [e]	15			8.22		
	DL-leucine	dioxane	*n*-hexylamine	35 °C	- [e]	10			6.17		
	DL-valine	dioxane	*n*-hexylamine	35 °C	- [e]	22.5			3.26		
	DL-valine	dioxane	*n*-hexylamine	35 °C	- [e]	15			2.33		
	2-amino-isobutyric acid	dioxane	*n*-hexylamine	35 °C					Too slow to measure		
6	DL-leucine	nitrobenzene	oligomer of DL-leucine	25.2 °C	- [e]	- [e]			41.7		
	DL-leucine	nitrobenzene	oligomer of DL-leucine	45 °C	- [e]	- [e]			87.2		
	DL-leucine	*o*-nitroanisole	oligomer of DL-leucine	25 °C	- [e]	- [e]			23.8		
	DL-leucine	*o*-nitroanisole	oligomer of DL-leucine	45 °C	- [e]	- [e]			58.3		
	DL-phenylalanine	nitrobenzene	oligomer of DL-phenylalanine	25 °C	- [e]	- [e]			15.6		
	DL-phenylalanine	nitrobenzene	oligomer of DL-phenylalanine	45 °C	- [e]	- [e]			35		
7	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.093	3			15		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.03	3.1			15		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.03	5			22		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.046	9.5			16		The NCA was synthesized from carbobenzoxy derivative

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
7	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.151	34			12		The NCA was synthesized from carbobenzoxy derivative
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.151	34			25		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_4$	25 °C	0.037	3.2			12		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_5$	25 °C	0.05	10			10		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_5$	25 °C	0.061	12			19		The NCA was synthesized from carbobenzoxy derivative
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_5$	25 °C	0.075	18			18		The NCA was synthesized from carbobenzoxy derivative
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_5$	25 °C	0.04	40			14		The NCA was synthesized from carbobenzoxy derivative
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_5$	25 °C	0.042	40			10		The NCA was synthesized from carbobenzoxy derivative
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_{15}$	25 °C	0.0382	3.1			24		The NCA was synthesized by phosgenation
	γ-benzyl L-glutamate	dioxane	poly (γ-benzyl L-glutamate)$_{15}$	25 °C	0.0374	3.7			18		The NCA was synthesized by phosgenation
8	sarcosine	acetophenone	dimethylamine	25 °C	0.17	12.75			263		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	12.75			258		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	12.75			245		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	8.5			179		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	k_2 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	Notes
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	8.5			197		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	6.375			137		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	6.375			122		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	6.375			143		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	4.25			111		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	4.25			100		
	sarcosine	acetophenone	dimethylamine	25 °C	0.17	1.16			67		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	12.75			235		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	12.75			239		
8	sarcosine	acetophenone	dimethylamine	45 °C	0.17	8.5			185		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	8.5			191		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	8.5			217		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	4.25			147		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	4.25			142		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	1.16			97.5		
	sarcosine	acetophenone	dimethylamine	45 °C	0.17	1.16			100		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	12.3			238		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	12.3			248		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	8.22			182		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	sarcosine	dioxane	dimethylamine	25 °C	0.24	8.22			184		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	4.11			105		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	4.11			105		
	sarcosine	dioxane	dimethylamine	25 °C	0.24	1.54			56		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	15.5			275		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	15.5			282		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	15.5			392		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	15.5			254		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	10.3			247		
8	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	10.3			237		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	10.3			184		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	10.3			195		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	5.17			133		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	5.17			131		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	5.17			139		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	5.17			128		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	3.1			84		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	3.1			144		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	3.1			124		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.13	3.1			92		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	15.5			233		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	15.5			263		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	15.5			266		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	15.5			247		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	10.3			210		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	10.3			235		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	10.3			151		
8	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	10.3			258		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	5.17			156		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	5.17			193		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	5.17			178		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	5.17			178		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	3.1			104		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	3.1			136		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	3.1			126		
	sarcosine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	50 °C	0.13	3.1			164		
9	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.0595	21			21.17		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.120	8.5			22.83		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.16	2.1			21.83		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.194	4.2			20.67		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.096	6.8			40.33		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.096	18			93		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.135	18			86.67		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.161	1.8			26.5		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.089	6.8			49		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.141	3.4			50		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.035	12.5			25		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.07	3.3			20.33		
9	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.076	6.5			21.16		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.129	6.5			27.5		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.039	- [e]	LiCl	0.177	17.83		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.079	- [e]	LiCl	0.105	19.17		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.131	- [e]	3-methyl-imidazolidine-2,4-dione	0.055	36.33		
	sarcosine	dimethylformamide	preformed polysarcosine	25 °C	0.163	- [e]	3-methyl-imidazolidine-2,4-dione	0.073	50.67		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.037	- [e]	LiCl	0.229	29.17		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.053	- [e]	LiCl	0.11	22.67		
	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.058	- [e]	3-methyl-imidazolidine-2,4-dione	0.232	68		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
9	sarcosine	dimethylformamide	preformed polysarcosine	0 °C	0.042	- [e]	3-methyl-imidazolidine-2,4-dione	0.116	43.33		
10	γ-benzyl L-glutamate	chloroform	acetic acid	30 °C	0.107	53.5			1.08	8.97	
11	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	34 °C	0.15	37.98			9.5		Measured by infrared spectroscopy
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	34 °C	0.15	15.19			7.3	25	Measured by infrared spectroscopy
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	34 °C	0.15	7.60			8.0	31	Measured by infrared spectroscopy
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	34 °C	0.15	3.80			7.0	44	Measured by infrared spectroscopy
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	34 °C	0.15	1.90			6.9	52	Measured by infrared spectroscopy
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.15	15.19			5.1	23	Measured by carbon dioxide evolution method
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.15	7.60			4.7	34	Measured by carbon dioxide evolution method
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.15	3.80			4.9	47	Measured by carbon dioxide evolution method
12	L-leucine	dioxane	*n*-hexylamine	25 °C	0.134	6.6			13	90	
	γ-benzyl L-glutamate	nitrobenzene	*n*-hexylamine	25 °C	0.15	7.60			21	110	
	γ-benzyl L-glutamate	ethylene chloride	*n*-hexylamine	25 °C	0.15	7.60			15	140	
	γ-benzyl L-glutamate	chloroform	*n*-hexylamine	25 °C	0.15	7.60			45	300	
	γ-benzyl L-glutamate	benzene	*n*-hexylamine	25 °C	0.15	7.60			62	310	
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.15	7.60			6	32	

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
12	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	37.98			7.4		
	γ-benzyl D-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	37.98			7.1		
	γ-benzyl DL-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	37.98			5.1		
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	7.60			5.5		
	γ-benzyl D-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	7.60			5.6	32	
	γ-benzyl DL-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.15	7.60			7.4	34	
13	γ-benzyl L-glutamate	nitrobenzene	sodium methoxide	25 °C	0.15	1.52			1100		
	γ-benzyl L-glutamate	ethylene chloride	sodium methoxide	25 °C	0.15	1.52			4200		
	γ-benzyl L-glutamate	ethylene chloride	sodium methoxide	25 °C	0.15	1.52			4000		
	γ-benzyl L-glutamate	ethylene chloride	sodium methoxide	25 °C	0.15	0.38			1100		
	γ-benzyl L-glutamate	benzene	sodium methoxide	25 °C	0.038	0.38			29500		
	γ-benzyl L-glutamate	benzene	sodium methoxide	25 °C	0.038	0.38			38000		
	γ-benzyl L-glutamate	benzene	sodium methoxide	25 °C	0.038	0.095			18000		
	γ-benzyl L-glutamate	benzene	sodium methoxide	25 °C	0.038	0.095			20000		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	15 °C	0.15	3.80			5400		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	25 °C	0.15	3.80			7400		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	15 °C	0.15	1.52			6300		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	25 °C	0.15	1.52			6000		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
13	γ-benzyl L-glutamate	dioxane	sodium methoxide	40 °C	0.15	1.52			5100		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	15 °C	0.15	0.38			5300		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	25 °C	0.15	0.38			5800		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	25 °C	0.15	0.15			4400		
	γ-benzyl L-glutamate	dioxane	sodium methoxide	40 °C	0.15	0.15			6400		
14	glycine	dioxane	*p*-bromoaniline	37 °C	0.2	0.4-12.8			1.8		
15	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	30 °C	0.19	- [e]			7.5	18.3	
	γ-benzyl DL-glutamate	dioxane	*n*-hexylamine	30 °C	0.19	- [e]			5.7	9.4	
16	γ-benzyl L-glutamate	dioxane	bis-tributyltin oxide	29.8 °C	0.1	10			4	11.67	
	γ-benzyl L-glutamate	dioxane	dibutyltin dimethoxide.	30 °C	0.1	2			6.67	16.67	
	γ-benzyl L-glutamate	dioxane	dibutyltin dimethoxide.	30 °C	0.1	4			5	22.08	
	γ-benzyl L-glutamate	dioxane	dibutyltin dimethoxide.	30 °C	0.1	8			4.17	15	
	γ-benzyl L-glutamate	dioxane	dibutyltin dimethoxide.	30 °C	0.1	12.5			3.33	13.6	
	γ-benzyl L-glutamate	dimethylformamide	dibutyltin dimethoxide.	30 °C	0.1	2			35.33	20.83	
	γ-benzyl L-glutamate	dimethylformamide	dibutyltin dimethoxide.	30 °C	0.1	8			13.75	27	
17	sarcosine	nitrobenzene	*N,N*-diethyl-sarcosinamide	25 °C	0.1	5			54.67		
	sarcosine	nitrobenzene	diethylamine-polysarcosine$_5$	25 °C	0.1	5			32		
	sarcosine	nitrobenzene	diethylamine-polysarcosine$_{12}$	25 °C	0.1	5			36.67		
	sarcosine	nitrobenzene	*N,N*-dimethyl-DL-phenyl-alaninamide	25 °C	0.1	5			34		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	sarcosine	nitrobenzene	dimethylamine-poly (DL-phenylalanine)$_5$	25 °C	0.1	5			13.67		
	sarcosine	nitrobenzene	dimethylamine-poly (DL-phenylalanine)$_{12}$	25 °C	0.1	5			10.33		
	DL-phenylalanine	nitrobenzene	*N,N*-diethyl-sarcosinamide	25 °C	0.1	5			370		
	DL-phenylalanine	nitrobenzene	diethylamine-polysarcosine$_5$	25 °C	0.1	5			1513.33		
	DL-phenylalanine	nitrobenzene	diethylamine-polysarcosine$_{12}$	25 °C	0.1	5			3900		
	DL-phenylalanine	nitrobenzene	diethylamine-polysarcosine$_{10}$-*b*-poly (DL-phenylalanine)$_2$	25 °C	0.1	5			3760		
17	DL-phenylalanine	nitrobenzene	diethylamine-polysarcosine$_5$-*b*-poly (DL-phenylalanine)$_2$-*b*-polysarcosine$_5$	25 °C	0.1	5			3463.33		
	DL-phenylalanine	nitrobenzene	diethylamine-polysarcosine$_4$ -DL-phenyl-alaninyl-*b*-polysarcosine$_3$-DL-phenyl-alaninyl-*b*-polysarcosine$_3$	25 °C	0.1	5			2593.33		
	DL-phenylalanine	nitrobenzene	diethylamine-sarcosinyl-*b*- poly (DL-phenylalanine)$_2$-*b*-polysarcosine$_9$	25 °C	0.1	5			1650		
	DL-phenylalanine	nitrobenzene	diethylamine- poly (DL-phenylalanine)$_2$ -*b*-polysarcosine$_{10}$	25 °C	0.1	5			630		
	DL-phenylalanine	nitrobenzene	dimethylamine- poly (DL-phenylalanine)$_2$ -*b*-polysarcosine$_{10}$	25 °C	0.1	5			553.33		
	DL-phenylalanine	nitrobenzene	dimethylamine-poly (DL-phenylalanine)$_5$	25 °C	0.1	5			15.67		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
17	DL-phenylalanine	nitrobenzene	dimethylamine-poly (DL-phenylalanine)$_2$	25 °C	0.1	5			16.33		
	DL-phenylalanine	nitrobenzene	*N,N*-dimethyl-DL-phenyl-alaninamide	25 °C	0.1	5			28.67		
18	γ-benzyl L-glutamate	dimethylformamide	*n*-butylamine	25 °C	0.22	5.5			0.85		
	γ-benzyl D-glutamate	dimethylformamide	trimethylenediamine	25 °C	0.18	4.5			1.67		
19	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	20 °C	0.13	2.66			1242		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	10 °C	0.13	2.66			577		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	0 °C	0.13	2.66			365		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	-10 °C	0.13	2.66			212		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	-20 °C	0.13	2.66			94.3		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	-30 °C	0.13	2.66			54.1		
	β-benzyl L-aspartate	tetrahydrofuran	sodium methoxide	30 °C	0.16	3.21			6320		
	β-benzyl L-aspartate	tetrahydrofuran	sodium methoxide	20 °C	0.16	3.21			3390		
	β-benzyl L-aspartate	tetrahydrofuran	sodium methoxide	0 °C	0.16	3.21			630		
	δ-benzyl L-α-aminoadipate	tetrahydrofuran	sodium methoxide	0.2 °C	0.13	2.52			476		
	δ-benzyl L-α-aminoadipate	tetrahydrofuran	sodium methoxide	-10 °C	0.13	2.52			252		
	δ-benzyl L-α-aminoadipate	tetrahydrofuran	sodium methoxide	-20.2 °C	0.13	2.52			145		
	δ-benzyl L-α-aminoadipate	tetrahydrofuran	sodium methoxide	-30.2 °C	0.13	2.52			91		
	N-deuterated γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	20 °C	0.13	2.65			1143		
	N-deuterated γ-benzyl L-glutamate	tetrahydrofuran	sodium methoxide	0 °C	0.13	2.65			271		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
20	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02			41.67		
	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02	pyridine	1	37.5		
	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02	2,2'-bipyridine	1	69.17		
	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02	2,2'-bipyridine	0.02	37.08		
	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02	4,4'-bipyridine	1	26.67		
	DL-phenylalanine	nitrobenzene	*n*-hexylamine	35 °C	0.2	0.02	poly(2-vinylpyridine)	1	55.83		
21	*O-tert*-butyl-DL-serine	benzene	*n*-hexylamine	25 °C	0.053	2.67			143.51	6.86	
	O-tert-butyl-DL-serine	benzene	*n*-hexylamine	25 °C	0.11	5.34			180.96	3.43	
	O-tert-butyl-DL-serine	benzene	*n*-hexylamine	30 °C	0.053	2.67			143.52	11.86	
	O-tert-butyl-DL-serine	dichloromethane	*n*-hexylamine	25 °C	0.053	2.67			11.86		
	O-tert-butyl-DL-serine	dichloromethane	*n*-hexylamine	25 °C	0.053	1.07			8.89		
	O-tert-butyl-DL-serine	benzene	*n*-hexylamine	25 °C	0.053	1.34			64.89		
	O-tert-butyl-L-serine	benzene	poly (*O-tert*-butyl-DL-serine)$_{40}$	25 °C	0.018	0.89			41.18		
	O-tert-butyl-DL-serine	benzene	poly (*O-tert*-butyl-DL-serine)$_{40}$-*b*-poly (*O-tert*-butyl-L-serine)$_{20}$	25 °C	0.021	0.53			49.92	18.72	
	O-tert-butyl-DL-serine	benzene	*n*-hexylamine	30 °C	0.053	2.67			106.08		
	O-tert-butyl-L-serine	benzene	poly (*O-tert*-butyl-DL-serine)$_{20}$	30 °C	0.053	1.48			157.24	29.20	
	O-tert-butyl-DL-serine	benzene	poly (*O-tert*-butyl-DL-serine)$_{20}$-*b*-poly (*O-tert*-butyl-L-serine)$_{36}$	30 °C	0.021	3.34			114.81	19.97	

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
22	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0567	7.09			21.3	28.0	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0604	3.45			27.0	40.9	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0557	3.18			28.3	38.4	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.105	5.25			28.2	38.9	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0369	1.85			16.8	23.5	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0236	1.18			14.2	45.7	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0385	1.93			22.4	29.6	
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	25 °C	0.0469	1.17			7.7	17.3	
23	γ-benzyl L-glutamate	dimethylformamide	*n*-propylamine	20 °C	0.05	2.5			30.67	43.33	
	γ-benzyl L-glutamate	dimethylformamide	*n*-dodecylamine	20 °C	0.05	2.5			33.33	36.67	
	γ-benzyl L-glutamate	dimethylformamide	ethylenediamine	20 °C	0.05	2.5			30.67	60	
	γ-benzyl L-glutamate	dimethylformamide	1, 3-propylene-diamine	20 °C	0.05	2.5			30.67	68	
	γ-benzyl L-glutamate	dimethylformamide	octamethylenediamine	20 °C	0.05	2.5			34.67	75.33	
	γ-benzyl L-glutamate	dimethylformamide	decamethylenediamine	20 °C	0.05	2.5			36.67	74.67	
	γ-benzyl L-glutamate	dimethylformamide	dodecamethylenediamine	20 °C	0.05	2.5			36.67	73.33	
24	*p*-methoxy-DL-phenyl-alanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			338.67		
	p-methoxy-DL-phenyl-alanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			292		
	DL-phenyl-alanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			340		
	DL-phenyl-alanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			353.33		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	m-nitro-DL-phenylalanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			1314.67		
	m-nitro-DL-phenylalanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			1100		
	m-nitro-DL-phenylalanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			836		
	m-nitro-DL-phenylalanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			680		
	p-nitro-DL-phenylalanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			556		
	p-nitro-DL-phenylalanine	nitrobenzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	2.5			457.33		
	p-nitro-DL-phenylalanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			866.67		
	p-nitro-DL-phenylalanine	nitrobenzene	dimethylamine-polysarcosine$_{15}$	25 °C	0.05	2.5			918.67		
	p-nitro-DL-phenylalanine	dimethylformamide	poly (2-vinylpyridine)	35 °C	0.1	100			0.047		
24	*p*-nitro-DL-phenylalanine	dimethylformamide	α-picoline	35 °C	0.1	100			0.11-0.17		
	m-nitro-DL-phenylalanine	dimethylformamide	poly (2-vinylpyridine)	35 °C	0.1	100			0.046		
	m-nitro-DL-phenylalanine	dimethylformamide	α-picoline	35 °C	0.1	100			0.10-0.15		
	DL-phenyl-alanine	dimethylformamide	poly (2-vinylpyridine)	35 °C	0.1	100			0.13		
	DL-phenyl-alanine	dimethylformamide	α-picoline	35 °C	0.1	100			0.47		
	p-methoxy-DL-phenyl-alanine	dimethylformamide	poly (2-vinylpyridine)	35 °C	0.1	100			0.022		
	p-methoxy-DL-phenyl-alanine	dimethylformamide	α-picoline	35 °C	0.1	100			0.055		
	m-nitro-DL-phenylalanine	nitrobenzene	poly (2-vinylpyridine)	35 °C	0.1	100			0.4		
	m-nitro-DL-phenylalanine	nitrobenzene	α-picoline	35 °C	0.1	100			0.28-0.37		
	DL-phenyl-alanine	nitrobenzene	poly (2-vinylpyridine)	35 °C	0.1	100			0.13		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	DL-phenyl-alanine	nitrobenzene	α-picoline	35 °C	0.1	100			0.062-0.11		
	p-methoxy-DL-phenyl-alanine	nitrobenzene	poly (2-vinylpyridine)	35 °C	0.1	100			0.073		
	p-methoxy-DL-phenyl-alanine	nitrobenzene	α-picoline	35 °C	0.1	100			0.039-0.043		
	m-nitro-DL-phenylalanine	methyl benzoate	poly (2-vinylpyridine)	35 °C	0.1	100			0.52		
	m-nitro-DL-phenylalanine	methyl benzoate	α-picoline	35 °C	0.1	100			0.12-0.20		
	DL-phenyl-alanine	methyl benzoate	poly (2-vinylpyridine)	35 °C	0.1	100			0.048		
	DL-phenyl-alanine	methyl benzoate	α-picoline	35 °C	0.1	100			0.020		
	p-Methoxy-DL-phenyl-alanine	methyl benzoate	poly (2-vinylpyridine)	35 °C	0.1	100			0.026		
24	*p*-Methoxy-DL-phenyl-alanine	methyl benzoate	α-picoline	35 °C	0.1	100			0.018		
	p-nitro-DL-phenylalanine	acetophenone	poly (2-vinylpyridine)	35 °C	0.1	20			0.62		
	p-nitro-DL-phenylalanine	acetophenone	α-picoline	35 °C	0.1	20			0.40		
	m-nitro-DL-phenylalanine	acetophenone	poly (2-vinylpyridine)	35 °C	0.1	20			0.64		
	m-nitro-DL-phenylalanine	acetophenone	α-picoline	35 °C	0.1	20			0.20		
	DL-phenyl-alanine	acetophenone	poly (2-vinylpyridine)	35 °C	0.1	20			0.023		
	DL-phenyl-alanine	acetophenone	α-picoline	35 °C	0.1	20			0.073		
	p-methoxy-DL-phenyl-alanine	acetophenone	poly (2-vinylpyridine)	35 °C	0.1	20			0.15		
	p-methoxy-DL-phenyl-alanine	acetophenone	α-picoline	35 °C	0.1	20			0.085		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
25	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.152	3.8			7.0	44	
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.152	7.6			8.0	31	
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.152	3.8			5.4	34	Sweeping CO_2 out by N_2
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.152	7.6			6.2	32	Sweeping CO_2 out by N_2
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.126	4.05			3.8	34	N_2-stream over solution
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.131	4.3			1.8	13	N_2-stream through solution
	γ-benzyl L-glutamate	dioxane	*n*-hexylamine	25 °C	0.093	3.0			- [e]	15	Constant CO_2 pressure
26	L-phenylalanine	diethyl-formamide	benzylamine	25 °C	0.1	5			2.82	6.88	
	L-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	20			3.02	3.53	
	L-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	5			2.89	7.90	
	L-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	1			3.07	14.71	
	L-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	0.5			3.17	23.47	
27	L-phenylalanine	*m*-dimethoxy-benzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	0.05-0.1 [e]			157		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl glycinate	25 °C	0.05	0.05-0.1 [e]			98.2		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl L-alaninate	25 °C	0.05	0.05-0.1 [e]			6.65		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl L-phenylalaninate	25 °C	0.05	0.05-0.1 [e]			1.49		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl 2-aminopentanoate	25 °C	0.05	0.05-0.1 [e]			3.74		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl leucinate	25 °C	0.05	0.05-0.1 [e]			2.81		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl valinate	25 °C	0.05	0.05-0.1 [e]			1.79		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	L-phenylalanine	*m*-dimethoxy-benzene	diethyl L-aspartate	25 °C	0.05	0.05-0.1 [e]			1.13		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl D-phenylglycinate	25 °C	0.05	0.05-0.1 [e]			2.24		
	L-phenylalanine	*m*-dimethoxy-benzene	ethyl L-prolinate	25 °C	0.05	0.05-0.1 [e]			1.64		
	L-phenylalanine	*m*-dimethoxy-benzene	S-1-phenylethyl amine	25 °C	0.05	0.05-0.1 [e]			5.12		
	L-phenylalanine	*m*-dimethoxy-benzene	R-octan-2-amine	25 °C	0.05	0.05-0.1 [e]			1.58		
	D-phenylalanine	*m*-dimethoxy-benzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	0.05-0.1 [e]			184		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl glycinate	25 °C	0.05	0.05-0.1 [e]			106		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl L-alaninate	25 °C	0.05	0.05-0.1 [e]			6.44		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl L-phenylalaninate	25 °C	0.05	0.05-0.1 [e]			2.19		
27	D-phenylalanine	*m*-dimethoxy-benzene	ethyl 2-aminopentanoate	25 °C	0.05	0.05-0.1 [e]			5.45		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl leucinate	25 °C	0.05	0.05-0.1 [e]			5.37		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl valinate	25 °C	0.05	0.05-0.1 [e]			4.24		
	D-phenylalanine	*m*-dimethoxy-benzene	diethyl L-aspartate	25 °C	0.05	0.05-0.1 [e]			1.02		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl D-phenylglycinate	25 °C	0.05	0.05-0.1 [e]			2.37		
	D-phenylalanine	*m*-dimethoxy-benzene	ethyl L-prolinate	25 °C	0.05	0.05-0.1 [e]			1.48		
	D-phenylalanine	*m*-dimethoxy-benzene	S-1-phenyl-ethylamine	25 °C	0.05	0.05-0.1 [e]			2.39		
	D-phenylalanine	*m*-dimethoxy-benzene	R-octa*n*-2-amine	25 °C	0.05	0.05-0.1 [e]			2.09		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	0.05-0.1 [e]			5.72		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	ethyl L-alaninate	25 °C	0.05	0.05-0.1 [e]			0.934		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	ethyl leucinate	25 °C	0.05	0.05-0.1 [e]			0.205		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	ethyl valinate	25 °C	0.05	0.05-0.1 [e]			0.107		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	ethyl L-prolinate	25 °C	0.05	0.05-0.1 [e]			73.2		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	S-1-phenyl-ethylamine	25 °C	0.05	0.05-0.1 [e]			2.81		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	*N,N*-dimethyl-sarcosinamide	25 °C	0.05	0.05-0.1 [e]			5.54		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	ethyl L-alaninate	25 °C	0.05	0.05-0.1 [e]			1.80		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	ethyl leucinate	25 °C	0.05	0.05-0.1 [e]			1.15		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	ethyl valinate	25 °C	0.05	0.05-0.1 [e]			0.798		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	ethyl L-prolinate	25 °C	0.05	0.05-0.1 [e]			24.2		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	S-1-phenyl-ethylamine	25 °C	0.05	0.05-0.1 [e]			1.75		
27	*N*-methyl-L-alanine	nitrobenzene	(S)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.43		
	N-methyl-L-alanine	nitrobenzene	(R)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.23		
	N-methyl-L-alanine	nitrobenzene	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.37		
	N-methyl-L-alanine	nitrobenzene	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.18		
	N-methyl-DL-alanine	nitrobenzene	(S)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.29		
	N-methyl-DL-alanine	nitrobenzene	(R)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.3		
	N-methyl-DL-alanine	nitrobenzene	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.17		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	N-methyl-DL-alanine	nitrobenzene	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.05	tributylamine	0.05	0.12		
	N-methyl-L-alanine	dimethylformamide	(S)-3,5-dimethylimidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.22		
	N-methyl-L-alanine	dimethylformamide	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.18		
	N-methyl-L-alanine	dimethylformamide	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.16		
	N-methyl-D-alanine	dimethylformamide	(S)-3,5-dimethylimidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.13		
	N-methyl-D-alanine	dimethylformamide	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.12		
27	*N*-methyl-D-alanine	dimethylformamide	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	30 °C	0.1	0.2	triethylamine	1.42	0.092		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(R)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.1			0.41		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(R)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.05	triethylamine	0.05	0.38		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(R)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.05	triethylamine	0.05	0.56		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(S)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.1			0.33		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.05	triethylamine	0.05	0.21		
	(S)-(1-phenyl-ethyl)glycine	nitrobenzene	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.05	triethylamine	0.05	0.31		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(R)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	1.61		
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(R)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.27		
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(R)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	1.78		
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(S)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	1		
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.29		
	(S)-(1-phenyl-ethyl)glycine	acetonitrile	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	1.48		
27	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(R)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.93		
	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(R)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.29		
	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(R)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.65		
	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(S)-3,5-dimethylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.77		
	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(S)-5-benzyl-3-methylimidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.23		
	(S)-(1-phenyl-ethyl)glycine	dimethylformamide	(S)-5-isopropyl-3-methyl-imidazolidine-2,4-dione	25 °C	0.1	0.2	triethylamine	0.032	0.51		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	L-phenylalanine	diethyl-formamide	*N*-methyl-DL-alanine dimethylamide	25 °C	0.1	5			400		
	D-phenylalanine	diethyl-formamide	*N*-methyl-DL-alanine dimethylamide	25 °C	0.1	5			433.33		
	DL-phenylalanine	diethyl-formamide	*N*-methyl-DL-alanine dimethylamide	25 °C	0.1	5			236.67		
	L-phenylalanine	diethyl-formamide	sarcosine dimethylamide	25 °C	0.1	5			180		
	DL-phenylalanine	diethyl-formamide	sarcosine dimethylamide	25 °C	0.1	5			120		
	L-phenylalanine	diethyl-formamide	3-methyl-aminopropionic dimethylamide	25 °C	0.1	5			466.67		
	D-phenylalanine	diethyl-formamide	3-methyl-aminopropionic dimethylamide	25 °C	0.1	5			466.67		
28	DL-phenylalanine	diethyl-formamide	3-methyl-aminopropionic dimethylamide	25 °C	0.1	5			310		
	L-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	5			200		
	D-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	5			200		
	DL-phenylalanine	diethyl-formamide	*N*-methyl-benzylamine	25 °C	0.1	5			100		
	L-phenylalanine	diethyl-formamide	glycine dimethylamide	25 °C	0.1	5			160		
	D-phenylalanine	diethyl-formamide	glycine dimethylamide	25 °C	0.1	5			160		
	DL-phenylalanine	diethyl-formamide	glycine dimethylamide	25 °C	0.1	5			156.67		
	L-phenylalanine	*m*-dimethoxy-benzene	sarcosine dimethylamide	25 °C	0.05	31			89.25		
	D-phenylalanine	*m*-dimethoxy-benzene	sarcosine dimethylamide	25 °C	0.05	31			89.25		
	DL-phenylalanine	*m*-dimethoxy-benzene	sarcosine dimethylamide	25 °C	0.05	31			89.25		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	L-phenylalanine	*m*-dimethoxy-benzene	3-methyl-aminopropionic dimethylamide	25 °C	0.05	25			373.33		
	D-phenylalanine	*m*-dimethoxy-benzene	3-methyl-aminopropionic dimethylamide	25 °C	0.05	25			373.33		
	DL-phenylalanine	*m*-dimethoxy-benzene	3-methyl-aminopropionic dimethylamide	25 °C	0.05	25			386.67		
	L-phenylalanine	*m*-dimethoxy-benzene	*N*-methyl-benzylamine	25 °C	0.05	25			120		
	D-phenylalanine	*m*-dimethoxy-benzene	*N*-methyl-benzylamine	25 °C	0.05	25			133.33		
	DL-phenylalanine	*m*-dimethoxy-benzene	*N*-methyl-benzylamine	25 °C	0.05	25			120		
	L-phenylalanine	*m*-dimethoxy-benzene	sarcosine dimethylamide	25 °C	0.05	10			76.67		
	DL-phenylalanine	*m*-dimethoxy-benzene	sarcosine dimethylamide	25 °C	0.05	10			76.67		
28	L-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:1	sarcosine dimethylamide	25 °C	0.05	10			166.67		
	DL-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:1	sarcosine dimethylamide	25 °C	0.05	10			166.67		
	L-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:3	sarcosine dimethylamide	25 °C	0.05	10			273.33		
	DL-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:3	sarcosine dimethylamide	25 °C	0.05	10			173.33		
	L-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:7	sarcosine dimethylamide	25 °C	0.05	10			350		
	DL-phenylalanine	*m*-dimethoxy-benzene: nitro-benzene = 1:7	sarcosine dimethylamide	25 °C	0.05	10			196.67		
	L-phenylalanine	nitrobenzene	sarcosine dimethylamide	25 °C	0.05	10			566.67		
	DL-phenylalanine	nitrobenzene	sarcosine dimethylamide	25 °C	0.05	10			276.67		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	D-phenylalanine	*m*-dimethoxy-benzene	sarcosine diethylamide	25 °C	-[e]	-[e]			184		
	D-phenylalanine	*m*-dimethoxy-benzene	glycine ethylester	25 °C	-[e]	-[e]			106		
	D-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			6.44		
	D-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	-[e]	-[e]			2.19		
	D-phenylalanine	*m*-dimethoxy-benzene	L-norleucine ethyleste	25 °C	-[e]	-[e]			5.45		
	D-phenylalanine	*m*-dimethoxy-benzene	L-leucine ethylester	25 °C	-[e]	-[e]			5.37		
	D-phenylalanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			4.24		
	D-phenylalanine	*m*-dimethoxy-benzene	L-aspartic diethylester	25 °C	-[e]	-[e]			1.02		
	D-phenylalanine	*m*-dimethoxy-benzene	L-phenylglycine ethylester	25 °C	-[e]	-[e]			2.37		
29	D-phenylalanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			148		
	D-phenylalanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			23.9		
	D-phenylalanine	*m*-dimethoxy-benzene	(R)-2-octylamine	25 °C	-[e]	-[e]			209		
	L-phenylalanine	*m*-dimethoxy-benzene	sarcosine diethylamide	25 °C	-[e]	-[e]			157		
	L-phenylalanine	*m*-dimethoxy-benzene	glycine ethylester	25 °C	-[e]	-[e]			98.2		
	L-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			6.65		
	L-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	-[e]	-[e]			1.49		
	L-phenylalanine	*m*-dimethoxy-benzene	L-norleucine ethyleste	25 °C	-[e]	-[e]			3.74		
	L-phenylalanine	*m*-dimethoxy-benzene	L-leucine ethylester	25 °C	-[e]	-[e]			2.81		
	L-phenylalanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			1.79		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	L-phenylalanine	*m*-dimethoxy-benzene	L-aspartic diethylester	25 °C	-[e]	-[e]			1.13		
	L-phenylalanine	*m*-dimethoxy-benzene	L-phenylglycine ethylester	25 °C	-[e]	-[e]			2.2		
	L-phenylalanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			164		
	L-phenylalanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			51.2		
	L-phenylalanine	*m*-dimethoxy-benzene	(R)-2-octylamine	25 °C	-[e]	-[e]			158		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	sarcosine diethylamide	25 °C	-[e]	-[e]			55.0		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			1.80		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-leucine ethylester	25 °C	-[e]	-[e]			1.15		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	-[e]	-[e]			0.307		
29	*N*-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			0.798		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			24.2		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			1.75		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	(R)-α-phenethylamine	25 °C	-[e]	-[e]			2.20		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	(R)-2-octylamine	25 °C	-[e]	-[e]			54.2		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	sarcosine diethylamide	25 °C	-[e]	-[e]			57.2		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			0.934		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-leucine ethylester	25 °C	-[e]	-[e]			0.205		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	-[e]	-[e]			0.111		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			0.107		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			73.2		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			2.81		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	(R)-α-phenethylamine	25 °C	-[e]	-[e]			1.52		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	(R)-2-octylamine	25 °C	-[e]	-[e]			55.8		
	N-methyl-D-alanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			3.92		
	N-methyl-D-alanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			161		
	N-methyl-D-alanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			5.22		
	N-methyl-L-alanine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			0.461		
	N-methyl-L-alanine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			144		
29	*N*-methyl-L-alanine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			5.07		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			1.80		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-alanine sec-butylester	25 °C	-[e]	-[e]			3.07		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-alanine dimethylamide	25 °C	-[e]	-[e]			296		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-alanine ethylester	25 °C	-[e]	-[e]			0.943		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-alanine sec-butylester	25 °C	-[e]	-[e]			1.94		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-alanine dimethylamide	25 °C	-[e]	-[e]			222		
	N-methyl-D-leucine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			1.91		
	N-methyl-D-leucine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			97.7		
	N-methyl-D-leucine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			13.3		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
29	*N*-methyl-L-leucine	*m*-dimethoxy-benzene	L-valine ethylester	25 °C	-[e]	-[e]			1.42		
	N-methyl-L-leucine	*m*-dimethoxy-benzene	L-proline ethylester	25 °C	-[e]	-[e]			168		
	N-methyl-L-leucine	*m*-dimethoxy-benzene	(S)-α-phenethylamine	25 °C	-[e]	-[e]			30.1		
30	L-leucine	dimethylformamide	*N*-(6-amino-hexy1) carbamic acid	25 °C	0.1	0.5			3.29	12.9	Initial gas was nitrogen
	L-leucine	dimethylformamide	*N*-(6-amino-hexy1) carbamic acid	25 °C	0.1	1			3.06	12.1	Initial gas was nitrogen
	L-leucine	dimethylformamide	hexamethylenediamine	25 °C	0.1	0.5			2.64	13.4	Initial gas was nitrogen
	L-leucine	dimethylformamide	hexamethylenediamine	25 °C	0.1	0.5			2.40	13.3	Initial gas was carbon dioxide
	L-leucine	dioxane	hexamethylenediamine	25 °C	0.1	0.5			1.47	6.9	Initial gas was nitrogen
	L-leucine	dioxane	hexamethylenediamine	25 °C	0.1	0.5			1.06	5.4	Initial gas was carbon dioxide
31	DL-phenylalanine	nitrobenzene	SIP-1 [f]	40 °C	86.8	15.5			36		
	DL-phenylalanine	dioxane	SIP-2 [f]	40 °C	109.04	18.8			7.9		
	DL-phenylalanine	tetrahydrofuran	S2P-1 [f]	40 °C	74.1	13.0			2.9		
	DL-phenylalanine	nitrobenzene	M1P-1 [f]	40 °C	90.5	18.1			34		
	DL-phenylalanine	dioxane	M1P-2 [f]	40 °C	134.5	26.9			6.4		
	DL-phenylalanine	tetrahydrofuran	M2P-1 [f]	40 °C	72.22	15.7			4.6		
	γ-benzyl L-glutamate	nitrobenzene	S1M-1 [f]	40 °C	69.85	12.7			96		
	γ-benzyl L-glutamate	dioxane	S1M-2 [f]	40 °C	77.47	12.7			60		
	γ-benzyl L-glutamate	tetrahydrofuran	S1M-3 [f]	40 °C	59.4	13.2			20		
	γ-benzyl L-glutamate	nitrobenzene	M1M-1 [f]	40 °C	-[e]	-[e]			100		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	γ-benzyl L-glutamate	dioxane	M1M-2 [f]	40 °C	-[e]	-[e]			50		
	γ-benzyl L-glutamate	tetrahydrofuran	M2M-1 [f]	40 °C	-[e]	-[e]			27		
	L-valine	nitrobenzene	S2V-1 [f]	40 °C	-[e]	-[e]			14		
	L-valine	dioxane	S2V-2 [f]	40 °C	-[e]	-[e]			2.8		
	L-valine	tetrahydrofuran	S2V-3 [f]	40 °C	-[e]	-[e]			1.0		
	L-valine	nitrobenzene	M1V-1 [f]	40 °C	-[e]	-[e]			16		
	L-valine	tetrahydrofuran	M2V-1 [f]	40 °C	-[e]	-[e]			1.2		
31	DL-phenylalanine	nitrobenzene	S1P-1 [f]	40 °C	-[e]	-[e]			36		
	DL-phenylalanine	nitrobenzene	M1P-1 [f]	40 °C	-[e]	-[e]			34		
	γ-benzyl L-glutamate	nitrobenzene	S1M-1 [f]	40 °C	-[e]	-[e]			96		
	γ-benzyl L-glutamate	nitrobenzene	M1M-1 [f]	40 °C	-[e]	-[e]			100		
	L-valine	nitrobenzene	S2V-1 [f]	40 °C	93.6	14.4			14		
	L-valine	nitrobenzene	M1V-1 [f]	40 °C	91.63	18.7			16		
	DL-phenylalanine	nitrobenzene	benzylamine	40 °C	116	11.6			17		
	γ-benzyl L-glutamate	nitrobenzene	benzylamine	40 °C	-[e]	-[e]			45		
	L-valine	nitrobenzene	benzylamine	40 °C	158.41	21.7			8.9		
32	D-phenylalanine	nitrobenzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	75			21.3		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
	L-phenylalanine	nitrobenzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	75			23.7		
	D-phenylalanine	nitrobenzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	75			42.5		
	L-phenylalanine	nitrobenzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	75			36.3		
	D-phenylalanine	nitrobenzene	L-phenylalanine ethylester	25 °C	0.05	75			77.8		
	L-phenylalanine	nitrobenzene	L-phenylalanine ethylester	25 °C	0.05	75			59.4		
	N-methyl-D-phenylalanine	nitrobenzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			30.3		
32	*N*-methyl-L-phenylalanine	nitrobenzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			20.2		
	N-methyl-D-phenylalanine	nitrobenzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			18.4		
	N-methyl-L-phenylalanine	nitrobenzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			92.1		
	N-methyl-D-phenylalanine	nitrobenzene	L-phenylalanine ethylester	25 °C	0.05	50			38.4		
	N-methyl-L-phenylalanine	nitrobenzene	L-phenylalanine ethylester	25 °C	0.05	50			24.6		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			22.1		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	(R)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			12.4		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
32	*N*-methyl-D-phenylalanine	*m*-dimethoxy-benzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			15.4		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	(S)-phenyl-alanyl-(S)-phenylalanylmorpholine amide	25 °C	0.05	50			92.1		
	N-methyl-D-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	0.05	50			30.7		
	N-methyl-L-phenylalanine	*m*-dimethoxy-benzene	L-phenylalanine ethylester	25 °C	0.05	50			11.1		
33	γ-benzyl L-glutamate	dioxane	1 [f]	-[e]	-[e]	-[e]			5.0	20	
	γ-benzyl L-glutamate	dioxane	2 [f]	-[e]	-[e]	-[e]			5.0	13	
	γ-benzyl L-glutamate	dioxane	3 [f]	-[e]	-[e]	-[e]			6.2	12	
	γ-benzyl L-glutamate	dioxane	3 [f]	-[e]	-[e]	-[e]			6.6	32	
	γ-benzyl L-glutamate	dioxane	4 [f]	-[e]	-[e]	-[e]			20	30	
	γ-benzyl L-glutamate	dioxane	5 [f]	-[e]	-[e]	-[e]			- [e]	26	
	γ-benzyl L-glutamate	dioxane	6 [f]	-[e]	-[e]	-[e]			- [e]	24	
34	γ-methyl L-glutamate	dichloromethane	HAPENAlO^{i}Pr [f]	25 °C	0.5	10			10.28		
	γ-methyl L-glutamate	dichloromethane	HAPENAlOMe [f]	25 °C	0.5	10			20.83		
	γ-methyl L-glutamate	dioxane	HAPENAlO^{i}Pr [f]	25 °C	0.5	10			3.06		
	γ-methyl L-glutamate	dioxane	HAPENAlOMe [f]	25 °C	0.5	10			2.78		
35	N_6-*tert*-butoxycarbonyl-L-lysine	dimethylformamide	benzylamine	room temperature	0.2	50			31.33		
	N_6-*tert*-butoxycarbonyl-L-lysine	dimethylformamide	benzylamine	room temperature	0.2	10			61.17		
	N_6-*tert*-butoxycarbonyl-L-lysine	dimethylformamide	benzylamine	room temperature	0.2	2			112.5		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	γ-benzyl D-glutamate	tetrahydrofuran	5Ni(COD) [f]	20 °C	0.08	3.2			156.25		
	γ-benzyl L-glutamate	tetrahydrofuran	5Ni(COD) [f]	20 °C	0.08	3.2			156.25		
	γ-benzyl D-glutamate	tetrahydrofuran	(S)-8Ni(COD) [f]	20 °C	0.08	3.2			71.88		
	γ-benzyl L-glutamate	tetrahydrofuran	(S)-8Ni(COD) [f]	20 °C	0.08	3.2			50		
	γ-benzyl D-glutamate	tetrahydrofuran	(R)-8Ni(COD) [f]	20 °C	0.08	3.2			65.63		
	γ-benzyl L-glutamate	tetrahydrofuran	(R)-8Ni(COD) [f]	20 °C	0.08	3.2			87.5		
	γ-benzyl D-glutamate	tetrahydrofuran	9Ni(COD) [f]	20 °C	0.08	3.2			71.88		
	γ-benzyl L-glutamate	tetrahydrofuran	9Ni(COD) [f]	20 °C	0.08	3.2			65.63		
	γ-benzyl D-glutamate	tetrahydrofuran	10Ni(COD) [f]	20 °C	0.08	3.2			93.75		
36	γ-benzyl L-glutamate	tetrahydrofuran	10Ni(COD) [f]	20 °C	0.08	3.2			53.13		
	γ-benzyl D-glutamate	tetrahydrofuran	11Ni(COD) [f]	20 °C	0.08	3.2			131.25		
	γ-benzyl L-glutamate	tetrahydrofuran	11Ni(COD) [f]	20 °C	0.08	3.2			106.25		
	γ-benzyl D-glutamate	tetrahydrofuran	12Ni(COD) [f]	20 °C	0.08	3.2			118.75		
	γ-benzyl L-glutamate	tetrahydrofuran	12Ni(COD) [f]	20 °C	0.08	3.2			75		
	γ-benzyl D-glutamate	tetrahydrofuran	13a Ni(COD) [f]	20 °C	0.08	3.2			40.63		
	γ-benzyl L-glutamate	tetrahydrofuran	13a Ni(COD) [f]	20 °C	0.08	3.2			7.81		
	γ-benzyl D-glutamate	tetrahydrofuran	13b Ni(COD) [f]	20 °C	0.08	3.2			1.03		
	γ-benzyl L-glutamate	tetrahydrofuran	13b Ni(COD) [f]	20 °C	0.08	3.2			2.59		
	γ-benzyl D-glutamate	tetrahydrofuran	13c Ni(COD) [f]	20 °C	0.08	3.2			1.03		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
36	γ-benzyl L-glutamate	tetrahydrofuran	13c Ni(COD) [f]	20 °C	0.08	3.2			2.09		
	γ-benzyl D-glutamate	tetrahydrofuran	13d Ni(COD) [f]	20 °C	0.08	3.2			0.31		
	γ-benzyl L-glutamate	tetrahydrofuran	13d Ni(COD) [f]	20 °C	0.08	3.2			1.03		
	γ-benzyl D-glutamate	tetrahydrofuran	13e Ni(COD) [f]	20 °C	0.08	3.2			37.5		
	γ-benzyl L-glutamate	tetrahydrofuran	13e Ni(COD) [f]	20 °C	0.08	3.2			25		
37	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	room temperature	0.19	1.90			10.24		Nitrogen flow rate was 0 ml/min
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	room temperature	0.19	1.90			29.25		Nitrogen flow rate was 100 ml/min
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	room temperature	0.19	1.90			55.57		Nitrogen flow rate was 250 ml/min
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	room temperature	0.19	3.80			13.16		Nitrogen flow rate was 0 ml/min
	γ-benzyl L-glutamate	dimethylformamide	*n*-hexylamine	room temperature	0.19	3.80			55.57		Nitrogen flow rate was 100 ml/min
38	*N*-*n*-butylglycine	toluene	NHC1 [f]	50 °C	0.15	3			69.54		
	N-*n*-butylglycine	toluene	NHC2 [f]	50 °C	0.15	3			27.96		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	3			26.11		
	N-*n*-butylglycine	toluene	NHC4 [f]	50 °C	0.15	3			4.46		
	N-*n*-butylglycine	dimethylsulfoxide	NHC1 [f]	50 °C	0.15	3			7.05		
	N-*n*-butylglycine	dimethylsulfoxide	NHC2 [f]	50 °C	0.15	3			8.72		
	N-*n*-butylglycine	dimethylsulfoxide	NHC3 [f]	50 °C	0.15	3			7.81		
	N-*n*-butylglycine	dimethylsulfoxide	NHC4 [f]	50 °C	0.15	3			6.91		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	0.38			52.85		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	k_2 [c, d] (×10-^{3} L mol-^{1}·s-^{1})	Notes
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	0.75			45.93		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	1.5			30		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	2.0			28.06		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	4.3			26.61		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	5.0			26.72		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	6.0			23.19		
	N-*n*-butylglycine	toluene	NHC3 [f]	40 °C	0.15	3.0			23.39		
	N-*n*-butylglycine	toluene	NHC3 [f]	55 °C	0.15	3.0			38.24		
	N-*n*-butylglycine	toluene	NHC3 [f]	60 °C	0.15	3.0			47.41		
38	*N*-*n*-butylglycine	toluene	NHC3 [f]	70 °C	0.15	3.0			62.13		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	3.0			13.98		
	N-ethylglycine	toluene	NHC3 [f]	50 °C	0.15	3.0			38.06		
	N-propylglycine	toluene	NHC3 [f]	50 °C	0.15	3.0			25.37		
	N-allylglycine	toluene	NHC3 [f]	50 °C	0.15	3.0			13.98		
	N-*n*-butylglycine	toluene	NHC5 [f]	50 °C	0.15	3			28.80		
	N-*n*-butylglycine	toluene	NHC6 [f]	50 °C	0.15	3			40.09		
	N-*n*-butylglycine	toluene	NHC7 [f]	50 °C	0.15	3			45.56		
	N-*n*-butylglycine	toluene	NHC8 [f]	50 °C	0.15	3			61.02		
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	1.5			40.93		Pressure of nitrogen was 15 psi

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
38	*N*-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	1.5			46.48		Pressure of carbon dioxide was 60 psi
	N-*n*-butylglycine	toluene	NHC3 [f]	50 °C	0.15	1.5			51.11		Pressure of carbon dioxide was 120 psi
	N-*n*-butylglycine	dimethylsulfoxide	NHC3 [f]	50 °C	0.15	1.5			22.41		Pressure of nitrogen was 15 psi
	N-*n*-butylglycine	dimethylsulfoxide	NHC3 [f]	50 °C	0.15	1.5			20.74		Pressure of carbon dioxide was 60 psi
	N-*n*-butylglycine	dimethylsulfoxide	NHC3 [f]	50 °C	0.15	1.5			17.04		Pressure of carbon dioxide was 120 psi
39	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	1.58	4744.80		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	3.17	1522.63		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	4.75	530.71		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	7.31	145.31		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	15.83	31.59		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	6.33	183.22		
40	*N*-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	3	1,1,3,3-tetramethylguanidine	0.00009	162.04		
	N-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	3			93.52		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
40	*N*-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	6	1,1,3,3-tetramethylguanidine	0.00009	173.15		
	N-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	1.5	1,1,3,3-tetramethylguanidine	0.00009	168.52		
	N-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	3	1,1,3,3-tetramethylguanidine	0.000045	150		
	N-*n*-butylglycine	tetrahydrofuran	benzyl alcohol	50 °C	0.15	3	1,1,3,3-tetramethylguanidine	0.00018	167.59		
41	N^{im}-trityl L-histidine	dimethylformamide	dimethylamine	room temperature	0.0031-0.21				18.77		
42	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethyl ethanolamine	25 °C	0.19	1.90	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	3.80	273.78	1189.89	
43	*N*-*n*-butylglycine	toluene	1,8-diazabicyclo-undec-7-ene	50 °C	0.15	1-6			39.67	84.17	
44 [g]	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.4	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.0032	3750		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.4	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.0063	3000		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.4	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.0095	2495.25		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.4	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.013	2323		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.4	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.032	- [e]	1572	
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	1.58	1,3-bis(2-hydroxyhexafluoro isopropyl) benzene	0.00158	10860.76		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
44 [g]	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.79	1,3-bis(2-hydroxyhexafluoroisopropyl) benzene	0.00158	8873.42		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.40	1,3-bis(2-hydroxyhexafluoroisopropyl) benzene	0.00158	7700		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.20	1,3-bis(2-hydroxyhexafluoroisopropyl) benzene	0.00158	4939		
	γ-benzyl L-glutamate	dichloromethane	*N,N*-dimethylethanolamine	room temperature	0.19	0.10	1,3-bis(2-hydroxyhexafluoroisopropyl) benzene	0.00158	2870		
45	γ-benzyl L-glutamate	tetrahydrofuran	potassium hexamethyldisilazide	room temperature	0.2	2			891.67		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium hexamethyldisilazide	room temperature	0.2	2			387.5		
	γ-benzyl L-glutamate	tetrahydrofuran	lithium hexamethyldisilazide	room temperature	0.2	2			234.72		
	γ-benzyl L-glutamate	tetrahydrofuran	sodium ethoxide	room temperature	0.2	2			40.28		
	γ-benzyl L-glutamate	tetrahydrofuran	triethylamine	room temperature	0.2	2			11.11		
	γ-benzyl L-glutamate	tetrahydrofuran	*n*-hexylamine	room temperature	0.2	2			9.72		
46 [g]	γ-benzyl L-glutamate	dichloromethane	1a [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1983.84		
	γ-benzyl L-glutamate	dichloromethane	1b [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1699.54		
	γ-benzyl L-glutamate	dichloromethane	1c [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1162.51		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	γ-benzyl L-glutamate	dichloromethane	1d [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	796.06		
	γ-benzyl L-glutamate	dichloromethane	1e [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	701.29		
	γ-benzyl L-glutamate	dichloromethane	1f [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1023.51		
	γ-benzyl L-glutamate	dichloromethane	1g [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1421.54		
	γ-benzyl L-glutamate	dichloromethane	2a [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	2419.78		
46 [g]	γ-benzyl L-glutamate	dichloromethane	2b [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1680.58		
	γ-benzyl L-glutamate	dichloromethane	2c [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	960.33		
	γ-benzyl L-glutamate	dichloromethane	2d [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1491.04		
	γ-benzyl L-glutamate	dichloromethane	2e [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	1206.73		
	γ-benzyl L-glutamate	dichloromethane	2f [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	417.64		
	γ-benzyl L-glutamate	dichloromethane	2g [f]	room temperature	0.19	1.58	N,N'-bis[3,5-bis(trifluoromethyl)phenyl] thiourea	0.0032	903.47		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
47	*N*-cyclohexyl-glycine	tetrahydrofuran	potassium hexamethyldisilazide	room temperature	0.2	2			24.58		
	N-cyclohexyl-glycine	tetrahydrofuran	sodium hexamethyldisilazide	room temperature	0.2	2			5.97		
	N-cyclohexyl-glycine	tetrahydrofuran	lithium hexamethyldisilazide	room temperature	0.2	2			4.86		
	N-cyclohexyl-glycine	tetrahydrofuran	*n*-hexylamine	room temperature	0.2	2			1.39		
48	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	-10 °C	- [e]	- [e]			0.972		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	-10 °C	0.17	3.4			1.01		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	-10 °C	0.43	8.6			0.94		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	-10 °C	0.59	11.8			0.96		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	-10 °C	- [e]	- [e]			1.095		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	0 °C	- [e]	- [e]			0.453		
	S-ethylsulfonyl-L-cysteine	dimethylformamide	neopentylamine	10 °C	- [e]	- [e]			0.262		
49 [g]	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	15	18-crown-6	0.003	9.33		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	24	18-crown-6	0.003	6.67		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30	18-crown-6	0.003	6.27		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	36	18-crown-6	0.003	6.25		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	45	18-crown-6	0.003	5.36		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30	18-crown-6	0.001	5.17		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30	18-crown-6	0.002	5.7		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30	18-crown-6	0.006	7.67		

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-3 L mol-1·s-1)	k_2 [c, d] (×10-3 L mol-1·s-1)	Notes
49 [g]	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30	18-crown*n*-6	0.009	9.13		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	15			4.73		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	24			4.38		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	30			4.07		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	36			3.58		
	γ-benzyl L-glutamate	chloroform	α,γ-dibenzyl-L-glutamate	25 °C	0.003	45			3.29		
50	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-$PBLG_{25}$ [f]	room temperature	0.05	2.0			62	1480000	
	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			72	215000	
	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-$PBLG_{100}$ [f]	room temperature	0.05	0.50			129	25500	
	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-$PBLG_{200}$ [f]	room temperature	0.05	0.25			167	7400	
	γ-benzyl L-glutamate	dichloromethane	P(NB_{50}-*r*-Ph_{50})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			34	1260000	
	γ-benzyl L-glutamate	dichloromethane	P(NB_{25}-*r*-Ph_{75})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			34	39200	
	γ-benzyl L-glutamate	dichloromethane	P(NB_{10}-*r*-Ph_{90})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			20	1200	
	γ-benzyl L-glutamate	dichloromethane	(PNB_{50}-*b*-PPh_{50})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			53	121000	
	γ-benzyl L-glutamate	dichloromethane	(PNB_{25}-*b*-PPh_{75})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			62	294000	
	γ-benzyl L-glutamate	dichloromethane	(PNB_{10}-*b*-PPh_{90})-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			54	7300	
	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-$PELG_{50}$ [f]	room temperature	0.05	1.0			140	5900	
	γ-benzyl L-glutamate	dichloromethane	PNB_{100}-*g*-P(EG_2-Lys)$_{50}$ [f]	room temperature	0.05	1.0			34	1710	
	γ-benzyl L-glutamate	chloroform	PNB_{100}-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			142	417000	

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
50	γ-benzyl L-glutamate	1,2-dichloroethane	PNB_{100}-*g*-$PBLG_{50}$ [f]	room temperature	0.05	1.0			81	32500	
	γ-benzyl L-glutamate	dichloromethane	$PBLG_{50}$ [f]	room temperature	0.05	1.0			13	90	
	γ-benzyl L-glutamate	dichloromethane	$PELG_{50}$ [f]	room temperature	0.05	1.0			26	440	
	γ-benzyl L-glutamate	dichloromethane	$P(EG_2\text{-Lys})_{50}$ [f]	room temperature	0.05	1.0			9.1	85	
51	γ-benzyl L-glutamate	dimethylsulfoxide	*n*-butylamine	5 °C	0.0767	1.53			9.1		
	γ-benzyl L-glutamate	dimethylsulfoxide	*n*-butylamine	-18 °C	0.0767	1.53			6.13		
52	γ-benzyl L-glutamate	tetrahydrofuran	lithium hexamethyldisilazide	room temperature	0.2	2			234.72		
	N_6-*tert*-butoxycarbonyl-DL-lysine	tetrahydrofuran	lithium hexamethyldisilazide	room temperature	0.2	2			5.83		
	γ-benzyl L-glutamate	tetrahydrofuran	bipyNi(COD) [f]	room temperature	0.2	2			120.83		
	γ-benzyl L-glutamate	tetrahydrofuran	*n*-hexylamine	room temperature	0.2	2			9.72		
53	γ-benzyl L-glutamate	dichloromethane	aniline	25 °C	0.75	15	(S)-1e [f]	0.375	150		
	γ-benzyl L-glutamate	dichloromethane	aniline	25 °C	0.75	15	(S)-1e [f]	0.75	69.78		
	γ-benzyl L-glutamate	dichloromethane	aniline	25 °C	0.75	15	(S)-1e [f]	1.125	68.67		
	γ-benzyl L-glutamate	dichloromethane	aniline	25 °C	0.75	15	(S)-1e [f]	1.5	40.33		
54 [g]	γ-benzyl L-glutamate	dichloromethane	*n*-hexylamine	room temperature	0.1	2			5.2	21	
	γ-benzyl L-glutamate	dichloromethane	ethylenediamine	room temperature	0.1	2			33	950	
	γ-benzyl L-glutamate	dichloromethane	tetramethylenediamine	room temperature	0.1	2			18	760	

(Continued)

Table SX (Continued)

Literature	Corresponding amino acid of AA-NCA monomer	Solvent	Initiator	Temperature	$[M_0]$ [b] (mol/L)	$[I_0]$ [b] (mmol/L)	Additives	[A] [b] (mol/L)	k_1 [c, d] (×10-[3] L mol-[1]·s-[1])	k_2 [c, d] (×10-[3] L mol-[1]·s-[1])	Notes
	γ-benzyl L-glutamate	dichloromethane	hexamethylenediamine	room temperature	0.1	2			20	780	
	γ-benzyl L-glutamate	dichloromethane	octamethylenediamine	room temperature	0.1	2			16	520	
	γ-benzyl L-glutamate	dichloromethane	decamethylenediamine	room temperature	0.1	2			15	410	
	γ-benzyl L-glutamate	dichloromethane	dodecamethylenediamine	room temperature	0.1	2			7.3	83	
	γ-benzyl L-glutamate	dichloromethane	ethylenediamine	room temperature	0.1	1			25	1500	
	γ-benzyl L-glutamate	dichloromethane	tetramethylenediamine	room temperature	0.1	1			18	1100	
54 [g]	γ-benzyl L-glutamate	dichloromethane	hexamethylenediamine	room temperature	0.1	1			17	950	
	γ-benzyl L-glutamate	dichloromethane	octamethylenediamine	room temperature	0.1	1			16	840	
	γ-benzyl L-glutamate	dichloromethane	decamethylenediamine	room temperature	0.1	1			15	540	
	γ-benzyl L-glutamate	dichloromethane	dodecamethylenediamine	room temperature	0.1	1			8.8	69	
	γ-benzyl L-glutamate	dichloromethane	hexamethylenediamine	room temperature	0.1	4			21	510	
	γ-benzyl L-glutamate	dichloromethane	hexamethylenediamine	room temperature	0.1	0.67			21	110	
	γ-benzyl L-glutamate	dichloromethane	hexamethylenediamine	room temperature	0.1	0.5			21	650	

[a] All the numbers quoted from the original text in this table are copied in the original format. For the calculated value, if less than 1, it is copied with two significant digits, if it is greater than 1, and its decimal part is less than two digits, it is copied directly, otherwise copied with two decimal places.

[b] $[M_0]$, $[I_0]$, [A] respectively represent the initial concentration of monomer, initiator, and additive.

[c] Since this table involves a large number of literatures, and the polymerization models used are different, only the apparent polymerization rate is used in order to avoid confusion. The apparent polymerization constants are calculated with the formula $k_{app} = k_p[I]$ (k_{app} represents the apparent monomer consumption rate, k_p represents apparent polymerization rate constant) and their conversion units are unified.

[d] Some literatures divide the polymerization process into two stages, so the rate constants of the two stages are both recorded. However, k_1 and k_2 between different papers do not necessarily refer to the same stage and cannot be compared with each other.

[e] This literature did not record the exact value.

f Here is the compound code in the original text. For the specific structure, please refer to the corresponding literature.

[g] Data in this article showed that the formula $k_{app} = k_p[I]$ is not valid in its polymerization system, and the calculated value in the table is for reference only.

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