Phosgene-Free Synthesis of Polypeptides: Useful Synthesis for Hydrophobic Polypeptides through Polycondensation of Activated Urethane Derivatives of α-Amino Acids

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Received 15 February 2013; accepted 7 May 2013; published online
DOI: 10.1002/pola.26775

ABSTRACT: We report a useful synthetic method of polypeptides using a series of urethane derivative of α-amino acids (L-leucine, L-phenylalanine, L-valine, L-alanine, L-isoleucine, L-methionine), which are readily synthesized by *N*-carbamoylation of tetrabutylammonium salts of α-amino acids with diphenyl carbonate. Heating these urethane derivatives in *N,N*-dimethylacetamide in the presence of *n*-butylamine successfully gave the corresponding polypeptides with well-defined structures through polycondensation with the elimination of phenol and CO_2. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry investigation showed that the resulting polypeptides had an *n*-BuNH_2-incorporated initiating end and an amino group at propagating end. These results strongly indicated that primary amines served as an initiator in this polycondensation system. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

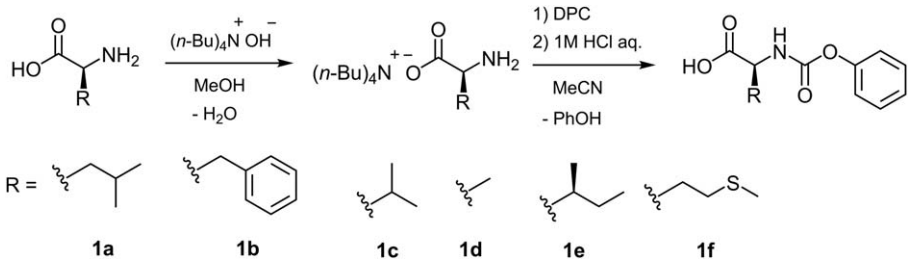
KEYWORDS: amino acid; monomers; polycondensation; polypeptide; ring-opening polymerization

INTRODUCTION Synthetic polypeptides have been widely used as important and essential components to design drug delivery system[1] and tissue engineering,[2] due to their desirable properties such as biocompatibility and biodegradability. For their applications, most polypeptides have been prepared by the ring-opening polymerization of α-amino acid *N*-carboxyanhydrides (NCAs). Polymerization of NCAs is generally initiated by various nucleophiles, such as water, alcohols, or primary amines. The initiation with primary amines is the most frequently used one to construct various architectures including block copolymers,[3] star-shaped polymers,[4] and hyperbranched polymers.[5] Furthermore, the remarkable feature of their polymerization is that molecular weight of polypeptides is precisely controlled by varying the feed ratio between monomers and initiators. However, in spite of the aforementioned advantages of NCAs, the sensitive nature of NCAs to moisture and heat has limited their use to the small-scale synthesis of polypeptides

Development of alternative procedures for polypeptide synthesis using more accessible monomers is a great challenge in this research area. To date, some researchers have reported various useful methods for polypeptide synthesis. Buess et al. developed α-carboxy hydroxamic acids that rearranged into isocyanate carboxylic acids with a potential capability to give corresponding polypeptides.[6] Orgel et al. used *N,N′*-carbonyldiimidazole for the polycondensation of α-amino acids in aqueous solution.[7] They proposed the *in-situ* formation of NCAs through intramolecular cyclization of *N*-(imidazolylcarbonyl) amino acids. Krichelforf et al. reported the utilization of a more stable compound, α-(*N*-aryloxycarbonyl)amino-ω-carboxylalkane, as a monomer for polyamide synthesis.[8] The proposed reaction mechanism involved the thermally induced elimination of ArOH from the urethane moiety to produce α-isocyanato-ω-carboxylalkane, which underwent the polyaddition with the elimination of CO_2.

We have previously reported a useful synthetic method for NCAs and polypeptides *via* intramolecular cyclization of *N*-aryloxycarbonylα-amino acids into corresponding NCAs.[9] Among their activated urethane-type derivatives of α-amino acids, *N*-(phenyloxycarbonyl) amino acids would be the most promising monomers toward practical use of polypeptide-based functional materials, because of easy handling of urethane derivatives and its simple procedure for polypeptides synthesis without the use and production of any toxic compounds. Recently, we showed polypeptides synthesis of poly-L-lysine with well-defined terminal structure using these urethane derivatives of amino acid in the presence of amine, and approaching for the synthesis of block copolypeptides.[10] In this article, we demonstrate a facile polypeptide synthesis from various amino acids with hydrophobic side chains

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Synthetic procedure for activated urethane derivatives of α-amino acids (**1a–1f**).

(L-leucine, L-phenylalanine, L-valine, L-alanine, L-isoleucine, L-methionine) to expand the scope of our polycondensation method with using activated urethane derivatives.

RESULTS AND DISCUSSION

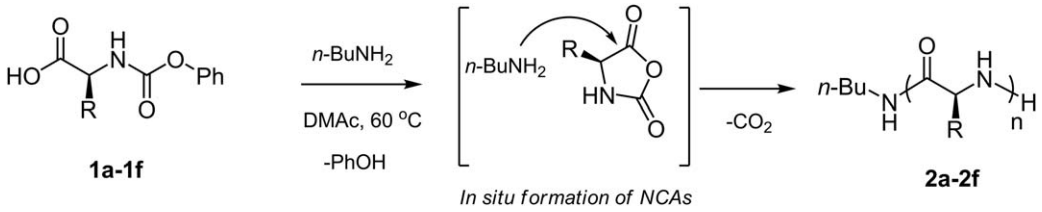
A series of activated urethane derivatives (**1a–1f**) for polypeptide synthesis were readily prepared by *N*-carbamoylation of tetrabutylammonium salts of α-amino acids with diphenyl carbonate (DPC) in acetonitrile, according to the method previously reported (Scheme 1).[10] As shown in Table 1, after purification with column chromatography and/or recrystallization, all urethane derivatives were successfully obtained in relatively high yields. These urethane derivatives are stable so that they could be stored at room temperature for several months without any caution to moisture and heat. The molecular structures of the obtained urethane derivatives were identified by ^{1}H NMR, ^{13}C NMR, and FTIR analyses.

In the previous report, we described that the activated urethane derivative of L-lysine efficiently gave polypeptide through the *in situ* formation of NCA and subsequent ring-opening polymerization in high polar solvents such as *N,N*-dimethylacetamide (DMAc), along with releasing phenol and carbon dioxide.[10] Furthermore, the addition of *n*-butylamine to the system gave the corresponding polypeptides with *n*-butylamine-incorporated initiating end (Scheme 2). Accordingly, we first investigated the polycondensation behavior of the urethane derivatives of L-leucine **1a** by heating their DMAc solution (0.5 M) at 60 °C in the absence of *n*-butylamine under argon atmosphere (entry 1 in Table 1). Aliquots of the reaction mixture were taken for monitoring the formation of phenol by ^{1}H NMR spectroscopy. After heating for 48 h, a small amount of precipitate was formed from the reaction mixture to suggest the formation of the target polypeptide. The resulting product was obtained as ether-insoluble parts (yield = 10%). The ^{1}H NMR spectrum measured at this point revealed low consumption of **1a** (conversion = 35%). Its FTIR spectrum (Fig. 1) indicated two characteristic peaks to amide linkage at 1648 and 1536 cm^{-1}, which are attributed to C═O stretching and N—H bending vibrations. Next, the effect of *n*-butylamine on this polycondensation system was investigated. In the presence of *n*-butylamine (2 mol %), the consumption of **1a** was significantly accelerated. ^{1}H NMR analysis showed the complete consumption of the urethane derivative within 28 h (entry 2 in Table 1) and the corresponding polypeptide was obtained in high yield (89%). This acceleration effect of *n*-butylamine was observed also in the previous study on the synthesis of poly-L-lysine.[10] Therefore, under same conditions, the polycondensation of urethane derivatives **1b–1f** were performed. The results are summarized in Table 2. During the polycondensation of **1a–1f,** precipitation or gelation was observed to suggest the formation of polypeptides in a β-sheet structure, which are generally insoluble in solvents. After pouring the reaction mixture into diethyl ether, the polypeptides were isolated as white powders in high yields. All the obtained polypeptides **2a–2f** were insoluble in common organic solvents, such as DMF, acetone, THF, and $CHCl_3$, but soluble in CF_3COOH (TFA). The insolubility of the obtained polypeptides in common organic solvents prevented the characterization with size exclusion chromatography. For the polycondensation of L-valine derivative **1c,** and L-isoleucine derivative **1e,** longer reaction times (over 50 h) were required for their complete consumption, compared to the other α-amino acids. The difference in polymerization time is likely due to the difference in rate of NCA formation that depends on steric hindrance of the substituent and the difference in solubility of the formed polypeptide.

Finally, we performed matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis of the polypeptide obtained by the polymerization from urethane derivatives in the presence of *n*-butylamine to confirm their molecular weight and the terminal structure. For the analysis, the polypeptide was dissolved in TFA, and mixed with 2,5-dihydroxybenzoic acid (2,5-DHB) and sodium trifluoroacetate (NaTFA) as a matrix and a cationization agent, respectively. The MALDI-TOF MS spectrum of poly-L-valine **2c** is shown in Figure 2 (for the spectra of other

TABLE 1 Synthesis of Urethane Derivatives from *N*-Carbamoylation of Tetrabutylammonium Salts of α-Amino Acids with Diphenyl Carbonates (DPC)

Entries	α-Amino Acid	Urethane Derivative	Yield (%)
1	Leucine	**1a**	70
2	Phenylalanine	**1b**	60
3	Valine	**1c**	58
4	Alanine	**1d**	62
5	Isoleucine	**1e**	65
6	Methionine	**1f**	75



SCHEME 2 Polypeptides synthesis from urethane derivatives of α-amino acids in the presence of *n*-butylamine.

polypeptides see the Supporting Information). These signals were regularly located with an interval of 99 Da, which corresponds to the formula weight of L-valine, and polymerization degree of **2c** was confirmed to be distributed in the wide range from 10 to 40, presumably, due to the precipitation of polypeptides during the polycondensation. Furthermore, these mass numbers give close agreement with Na^+-cationized polymer structure, possessing *n*-butylamine-incorporated initiating end and $-NH_2$ group at propagating end. These polypeptide structures were completely similar to that synthesized by butylamine-initiated ring-opening polymerization of NCAs. In addition, ^1H NMR spectrum of **2c** (TFA-d_1) also provided the evidence for the existence of the butylamine reside on the terminal of polypeptide (Fig. 3). The butylamine residue was identified in the spectrum at 1.40, 1.61, and 3.45 ppm. These results strongly indicated *n*-butylamines serves as initiator in this polycondensation system. Thus, this polycondensation system would be a more facile alternative approach for synthesis of polypeptides by the initiation with amino groups. With this useful synthetic method for polypeptides synthesis, development of biocompatible materials is now in progress.

CONCLUSIONS

In this article, we proved that a series of urethane derivative of α-amino acids (L-leucine, L-phenylalanine, L-valine, L-alanine, L-isoleucine, L-methionine) has a potential to be used as monomers to facile synthesis of polypeptides with well-defined structure. These urethane derivatives were readily synthesized by two-step reactions, that is, (1) transformation of α-amino acids into the corresponding ammonium salts and (2) *N*-carbamoylation of the salts with DPC, and could be stored without any signs of decomposition for several months at room temperature. The polycondensation of these urethane derivatives was successfully carried out by heating them in DMAc in the presence of *n*-butylamine. The MALDI-TOF MS investigation showed that the resulting polypeptides have *n*-$BuNH_2$-incorporated initiating end and —NH_2 group at propagating end, implying that primary amines can serve as an initiator in this polycondensation system. Therefore, this polycondensation system would be conveniently used as a synthetic method of polypeptides with well-defined terminal structure.

EXPERIMENTAL

Materials and Instruments

All the reagents were purchased from Aldrich, Tokyo Chemical Industry, and Watanabe Chemical Industry, and used as received without further purification, unless stated otherwise. Butylamine (*n*-$BuNH_2$) and *N*,*N*-dimethylacetamide (DMAc) were purified by distillation over calcium hydride (CaH_2), before use. ^1H and ^{13}C NMR spectra were recorded with a JEOL ECS-400 (400 MHz) spectrometer, and chemical shifts were recorded in ppm units using tetramethylsilane as an internal standard. Fourier transform infrared spectroscopy (FTIR) analysis was recorded on Thermo Scientific Nicolet iS10 over a range from 600 to 4000 cm^{-1}. MALDI-TOF MS analysis was performed on a PerSeptive Biosystems Voyager DE Pro Bio Spectrometry workstation. The MALDI-TOF MS samples were prepared using 2,5-DHB and NaTFA, as a matrix material and a cationization agent, respectively. The polypeptides in TFA solution (5 mg mL^{-1}) was mixed with 2,5-DHB/THF solution (10 mg mL^{-1}) and NaTFA/THF solution (1 mg mL^{-1}) at a ratio of 1:2:1. The final mixed solutions were deposited onto a sample plate and allowed to air dry. The resulting samples were irradiated with 337 nm of nitrogen laser, and detected on positive mode at 20 kV. Melting point was measured on Bibby Stuart scientific melting point apparatus SMP3.

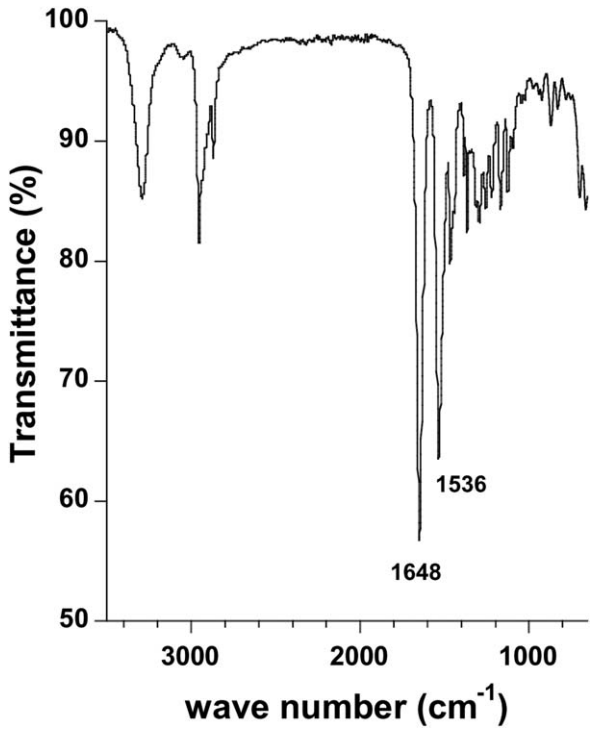


FIGURE 1 FT-IR spectrum of ether-insoluble part obtained by polycondensation of urethane derivatives **1a** (entry 1 in Table)

TABLE 2 Synthesis of Polypeptides from Urethane Derivatives (**1a–1f**) in the Presence of *n*-Butylamine (2 mol %)[a]

Entries	α-Amino Acid	Urethane Derivative	Polypeptide	Reaction Time (h)	Conv. (%)[c]	Yield (%)[d]
1[b]	Leucine	**1a**	**2a**	48	35	10
2	Leucine	**1a**	**2a**	28	>99	89
3	Phenylalanine	**1b**	**2b**	12	>99	85
4	Valine	**1c**	**2c**	50	>99	78
5	Alanine	**1d**	**2d**	36	>99	80
6	Isoleucine	**1e**	**2e**	72	>99	69
7	Methionine	**1f**	**2f**	18	>99	91

[a] Polycondensation condition: Conc. = 0.5 M, at 60 °C in DMAc.
[b] Polycondensation was performed in the absence of *n*-butylamine.
[c] Calculated by ^{1}H NMR spectra in $CDCl_3$.
[d] Ether-insoluble parts.

General Procedure for Synthesis of Various Urethane Derivatives

N-*Phenoxycarbonyl-L-leucine (1a)*

To a stirred suspension of L-leucine (2.6 g, 20 mmol) in methanol (30 mL), tetrabutylammonium hydroxide (37% in methanol) (13.8 g, 20 mmol) was slowly added at room temperature. After stirring for 1 h, the reaction mixture was concentrated under reduced pressure. The resulting residues were dissolved in acetonitrile (20 mL). The solution was added dropwise over 10 min to a stirred solution of DPC (4.2 g, 20 mmol) in acetonitrile (25 mL) at ambient condition, and then the reaction mixture was stirred for 3 h. The resulting mixture was transferred into a separatory funnel containing distilled water (30 mL) and ethyl acetate (30 mL). The aqueous layer was acidified to pH 2–3 with 1 M HCl and extracted with ethyl acetate (3 × 30 mL). The organic fractions were combined, washed with brine, dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The crude products were purified by flash column chromatography (eluting with a gradient from 30 to 60% ethyl acetate in *n*-hexane), and then recrystallization from ethyl acetate/*n*-hexane to give 3.5 g (70%) of **1a** as colorless oil.

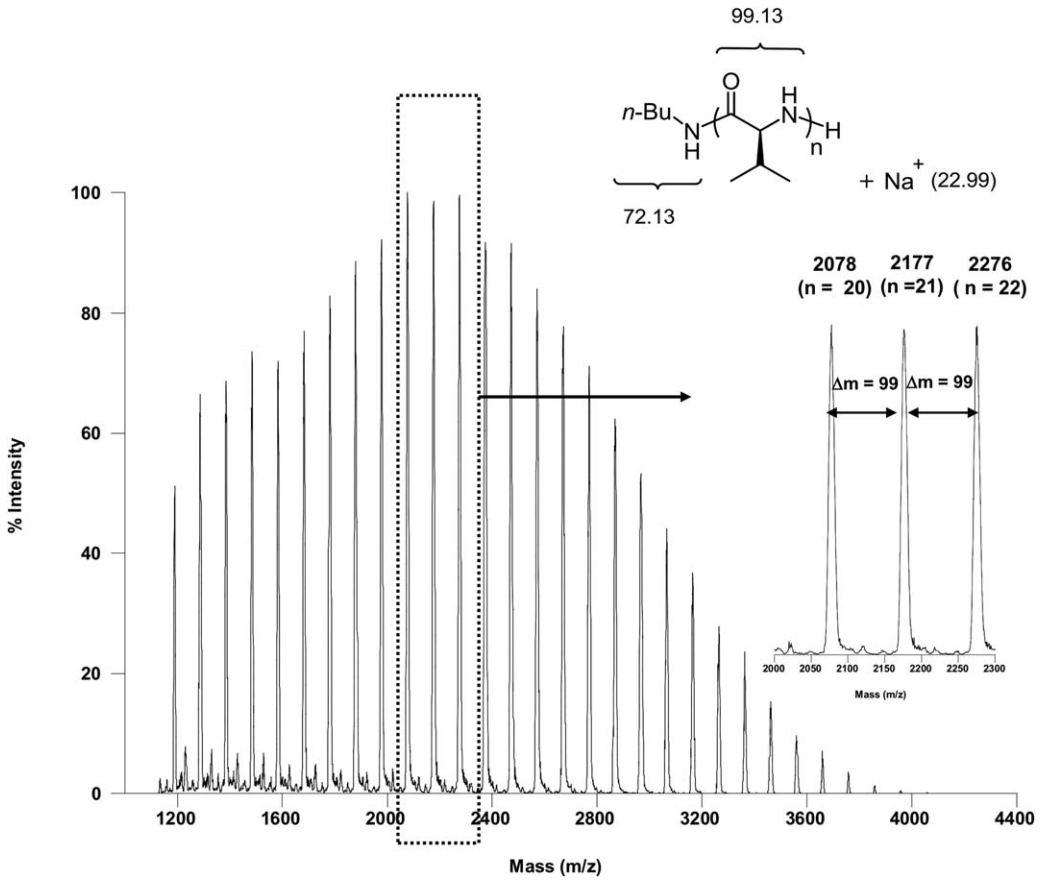


FIGURE 2 MALDI-TOF MS spectrum of poly-L-valine **2c** obtained from polycondensation of urethane derivatives in the presence of *n*-butylamine (entry 4 in Table 2).

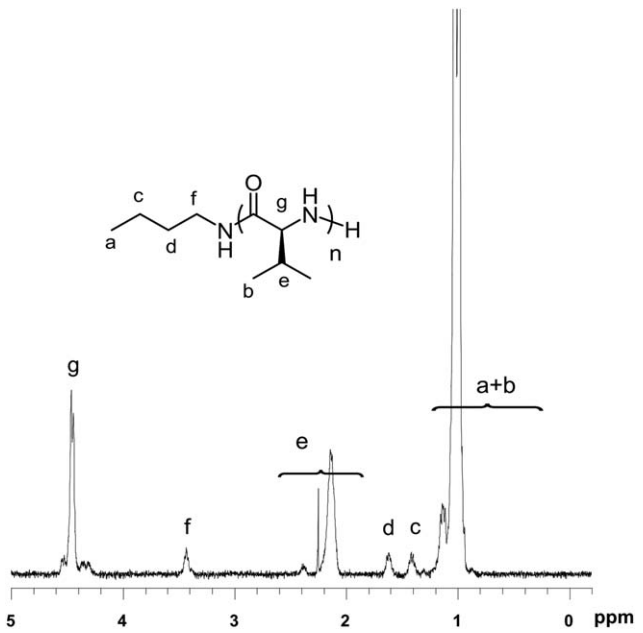


FIGURE 3 ^{1}H NMR spectrum of poly-L-valine **2c** in TFA-d.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.86–1.09 (m, 6H), 1.55–1.91 (m, 3H), 4.37–4.51 (m, 1H), 5.60 (d, 1H, J = 8.6 Hz), 7.06–7.25 (m, 3H), 7.28–7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 21.80, 22.49, 24.92, 41.50, 52.66, 121.66, 125.65, 129.41, 150.83, 154.70, 177.94. IR (neat, cm^{-1}): 3309, 2958, 1710, 1527, 1488, 1203, 1155, 1024, 686.

N-Phenoxycarbonyl-L-phenylalanine (1b)

The urethane derivative **1b** was prepared from L-phenylalanine, according to the procedure described above and was obtained as white powder in 60% yield, mp: 102.3–103.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.00–3.35 (m, 2H), 4.73 (m, 1H), 5.51 (d, 1H, J = 8.2 Hz), 7.07 (d, 2H, J = 7.7 Hz), 7.16–7.25 (m, 3H), 7.27–7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 37.77, 54.84, 121.62, 125.73, 127.50, 128.90, 129.46, 129.48, 135.43, 150.74, 154.32, 176.32. IR (neat, cm^{-1}): 3371, 3030, 1744, 1712, 1518, 1489, 1376, 1217, 1182, 751, 697.

N-Phenoxycarbonyl-L-valine (1c)

The urethane derivative **1c** was prepared from L-valine, according to the procedure described above and was obtained as colorless oil in 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.94–1.13 (m, 6H), 2.24–2.33 (m, 1H), 4.39 (m, 1H), 5.72 (d, 1H, J = 9.0 Hz), 7.05–7.22 (m, 3H), 7.31–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 17.51, 19.20, 31.25, 59.12, 121.63, 125.66, 129.44, 150.91, 154.85, 176.85. IR (neat, cm^{-1}): 3308, 2965, 1707, 1525, 1487, 1390, 1201, 1150, 760, 686.

N-Phenoxycarbonyl-L-alanine (1d)

The urethane derivative **1d** was prepared from L-alanine, according to the procedure described above and was obtained as white powder in 62% yield, mp: 112.0–112.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.50–1.60 (m, 3H), 4.42–4.54 (m, 1H), 5.66 (d, 1H, J = 7.6 Hz), 7.08–7.15 (m, 2H), 7.16–7.24 (m, 1H), 7.31–7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 18.47, 49.76, 121.67, 125.71, 129.46, 150.78, 154.27, 177.73. IR (neat, cm^{-1}): 3297, 2995, 1696, 1524, 1491, 1240, 1211, 1175, 1157, 687.

N-Phenoxycarbonyl-L-isoleucine (1e)

The urethane derivative **1e** was prepared from L-isoleucine, according to the procedure described above and was obtained as colorless oil in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.90–1.09 (m, 6H), 1.19–1.35 (m, 1H), 1.46–1.58 (m, 1H), 1.96–2.08 (m, 1H), 4.43 (dd, 1H, J = 8.8 Hz, J = 4.5 Hz), 5.64 (d, 1H, J = 8.8 Hz), 7.06–7.25 (m, 3H), 7.29–7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 11.74, 15.64, 24.99, 37.94, 58.50, 121.62, 125.62, 129.41, 150.88, 154.71, 176.89. IR (neat, cm^{-1}): 2964, 1707, 1523, 1487, 1384, 1200, 1149, 1023, 758, 686.

N-Phenoxycarbonyl-L-methionine (1f)

The urethane derivative **1f** was prepared from L-methionine, according to the procedure described above and was obtained as white powder in 75% yield, mp: 69.5–70.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.02–2.18 (m, 4H), 2.19–2.31 (m, 1H), 2.55–2.69 (m, 2H), 4.58 (m, 1H), 5.85 (d, 1H, J = 8.1 Hz), 7.08–7.15 (m, 2H), 7.17–7.23 (m, 1H), 7.31–7.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 15.52, 30.04, 31.47, 53.29, 121.62, 125.75, 129.46, 150.75, 154.62, 176.57. IR (neat, cm^{-1}): 3330, 2911, 1701, 1520, 1490, 1421, 1286, 1239, 1210, 1186, 1025, 777, 685.

Synthesis of Polypeptides by Polycondensation of Urethane Derivatives

Typical procedure is as follows: urethane derivatives of L-leucine **1a** (251 mg, 1.0 mmol) were dissolved in dry DMAc (2 mL), and added into a Schlenk tube. After addition of *n*-$BuNH_2$/DMAc solution (20 μL, 1.0 $\times$ 10^{-3} mmol μL^{-1}), the polycondensation was performed at 60 °C under argon atmosphere. The reaction mixture was cooled to room temperature and poured into diethyl ether. The precipitated polypeptides were isolated by filtration, and then dried under vacuum to yield 125 mg (85%), as white powder of **2a:** IR (neat, cm^{-1}): 3291, 2955, 2869, 1648, 1536, 1467, 1365.

Other polypeptides were also obtained as a white powder and the physical data of other polypeptides are listed below. **2b:** IR (neat, cm^{-1}): 3282, 1659, 1630, 1519, 1494, 744, 696. **2c:** IR (neat, cm^{-1}): 3269, 2961, 1628, 1547, 1390, 1226, 710. **2d:** IR (neat, cm^{-1}): 3271, 2980, 2936, 1625, 1528, 1448, 1377, 1304, 1160, 1104, 1048, 964, 890. **2e:** IR (neat, cm^{-1}): 3265, 2961, 1624, 1544, 1222, 1154, 719. **2f:** IR (neat, cm^{-1}): 3280, 2912, 1645, 1536, 1433, 1282, 1111.

ACKNOWLEDGEMENT

This work was financially supported by JSR Corporation.

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