Synthesis and Radical Ring-Opening Polymerization of Vinylcyclopropanes Derived from Amino Acids with Hydrophobic Moieties

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Received 16 August 2017; accepted 9 September 2017; published online 00 Month 2017
DOI: 10.1002/pola.28861

ABSTRACT: Six 1,1-disubstituted vinylcyclopropanes (VCP) were synthesized from glycine and amino acids bearing hydrophobic moieties, L-alanine, L-valine, L-leucine, L-isoleucine, and L-phenylalanine. These VCP derivatives efficiently underwent radical ring-opening polymerization to afford the corresponding polymers bearing *trans*-vinylene moiety in the main chains and the amino acid-derived chiral moieties in the side chains. The polymers were film-formable, and in the films of polymers bearing the glycine- and alanine-derived side chains, presence of hydrogen bonding was confirmed by IR analysis. Thermogravimetric analysis of the polymers revealed that the temperatures of 5% weight loss were higher than 300 °C. Differential scanning calorimetry clarified that the polymers were amorphous ones showing glass transition temperatures in a range of 48–80 °C. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

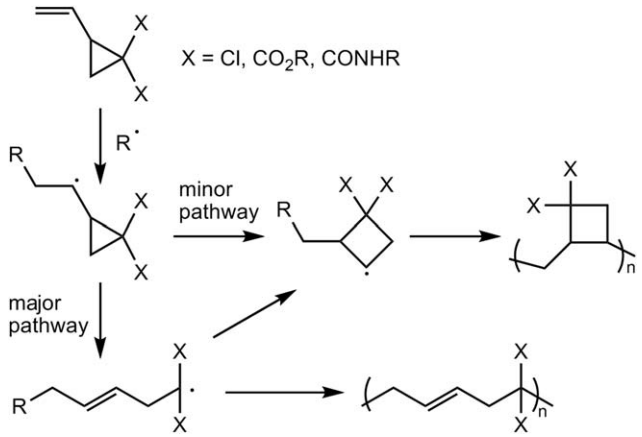
KEYWORDS: amino acid; radical ring-opening polymerization; vinylcyclopropane

INTRODUCTION Radical ring-opening polymerization (RROP) is one of the attractive methods to synthesize functional polymers bearing heteroatoms and functional groups in their main chains. In general, monomers that undergo RROP efficiently fulfill the following four requirements:[1] (1) Monomers should have a C—C double bond which can accept radical species. (2) They should have distorted ring structures. (3) Preferably, their ring-opening reactions accompany isomerization processes to form thermodynamically more stable structures. (4) The ring-opening reaction results in formation of radicals that can be stabilized by appropriately chosen and located functional groups.

Vinylcyclopropane (VCP) derivatives have attracted considerable attention as cyclic monomers undergoing RROP.[1–6] Among various VCPs, 1,1-disubstituted ones have been investigated most extensively. Their RROPs give the corresponding polymers bearing C—C double bonds in the main chains, often accompanied by a side reaction giving cyclobutane rings (Scheme 1). The successful RROP of these VCPs arise from the high distortion energy of cyclopropane ring and stabilization of the resulting radical by the two substituents at 1-position such as halogen and ester moieties. Controlled RROPs of VCP derivatives have been also achieved by nitroxide-mediated polymerizations in the presence of 2,2,6,6-tetramethylpiperidin-1-oxyl,[7] by using the reversible addition-fragmentation chain transfer protocol,[8] and using the atom transfer radical polymerization protocol.[9] In addition, copolymerizations with allylic carbonate,[10] methyl acrylate,[11] and other VCPs[12] have been reported. The copolymerization with methyl methacrylate afforded the corresponding polymer bearing cycloalkane moieties in the main chain. There have been reports on relatively low volume shrinkage accompanying the RROP of VCPs, which makes VCPs attractive as potential monomers applicable to coating, holographic data storages, and dental materials.[13–16]

Recently, RROPs of VCPs bearing amide moieties at 1-position have been reported.[15,16] Interestingly, the polymerizations were accelerated by hydrogen bonds between amide moieties. 1,1-Disubstituted VCP derivatives, on which α-amino acid-derived components are attached through amide

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



SCHEME 1 RROP system of VCP derivatives.

bonds, are monomers of high interest, because they can be used for synthesis of functionalized polymers with optically active nature[17–20] and C—C double bonds in the main chain that can be chemically modified by various methods.[21,22]

Herein, we report 1,1-disubstituted VCP monomers **1a**-**1f** bearing (*L*)-amino acid-derived moieties (Fig. 1). Among various amino acids, glycine and α-alkyl-substituted ones such as alanine, valine, leucine, isoleucine, and phenylalanine were selected and used. The polymerization behaviors of **1a**–**1f** were studied to find dependence on the structures of each amino acid moiety. These corresponding polymers have chirality arising from amino acid and ester parts available for postmodification.

RESULTS AND DISCUSSION

Synthesis of VCP Derivatives

Scheme 2 shows the route for the synthesis of the VCP derivatives **1a**–**1f**. Previously, we reported the synthesis of L-alanine-derived VCP **1b** in this route.[23] 1,1-Diethoxycarbonyl-2-vinylcyclopropane (DECVCP), which was synthesized by the reaction of diethyl malonate with 1,4-dibromobutene, was used as the starting material. Its ethyl esters were hydrolyzed under basic conditions and subsequent acidification with hydrochloric acid to yield 1,1-dicarboxy-2-vinylcyclopropane (DCAVCP). In the final step, DCAVCP was

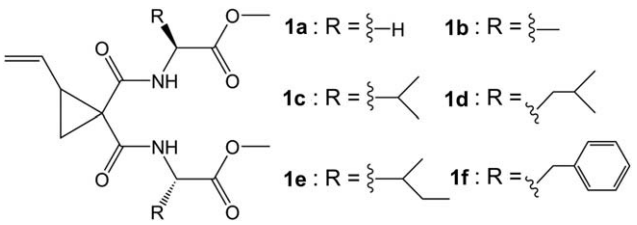
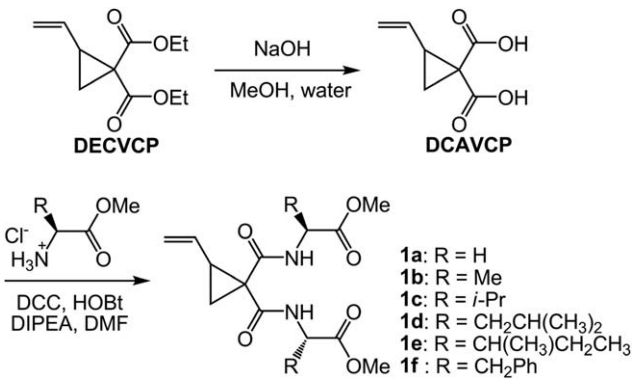


FIGURE 1 Molecular structures of VCPs bearing α-amino acid-derived moieties.



SCHEME 2 Synthesis of VCP derivatives **1**.

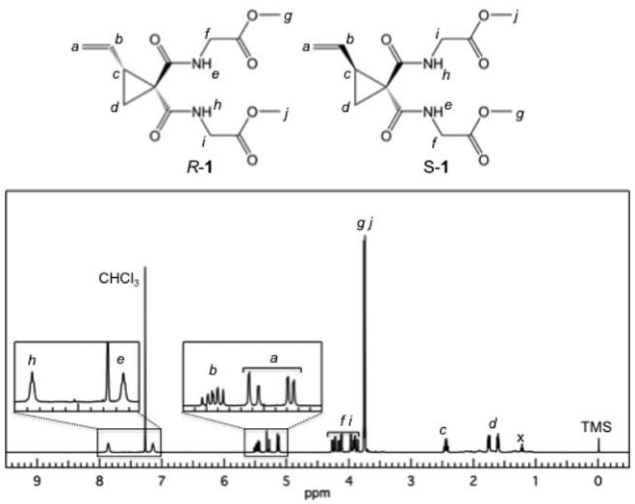


FIGURE 2 ^{1}H NMR spectrum of **1a** in $CDCl_3$.

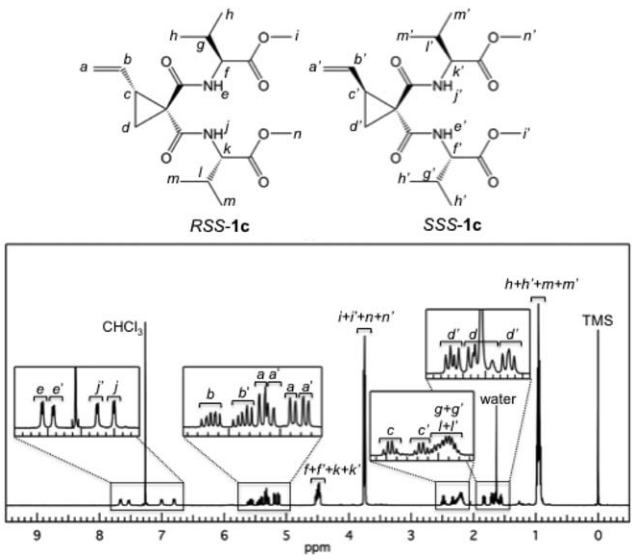
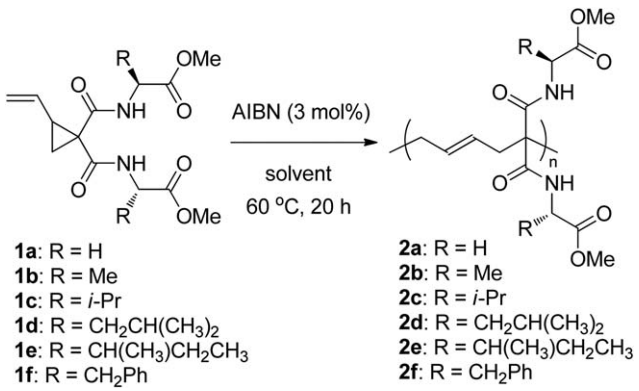


FIGURE 3 ^{1}H NMR spectrum of an epimeric mixture of **1c** (in $CDCl_3$).



SCHEME 3 RROP of **1**.

condensed with methyl esters of amino acids using *N*,*N*′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), and *N*,*N*-diisopropylethylamine (DIPEA) to afford the VCP derivatives **1**. Except the glycine-derived **1a**, the VCPs **1b-1e** bearing L-amino acid-derived moieties, were obtained as 1:1 epimeric mixtures.

Figure 2 shows the ^{1}H NMR spectrum of glycine-derived VCP **1a**. In the spectrum, the signals of the glycine-derived moiety in the *cis*-configuration to the vinyl moiety were distinguished from those of the other glycine-derived moiety in the *trans*-configuration to the vinyl moiety. For example, there are two signals at 7.9 and 7.2 ppm, which are attributable to the two amide protons *h* and *e*, respectively. For these assignments, we referred our previous investigation on the molecular structure of alanine-derived VCP **1b** by combining X-ray crystallography and NOE analysis, which clarified that the signal for the NH located in the *trans*-configuration to the vinyl moiety appeared in a lower magnetic field than that for the other NH located in the *cis*-configuration to the vinyl moiety.

Figure 3 shows the spectrum of L-valine-derived VCP **1c**, where the presence of two epimers *RSS*-**1c** and *SSS*-**1c** was confirmed. The signals were assigned as indicated in the Figure 3, according to the assignment made for the L-alanine-derived VCP **1b**. ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY analyses of **1c** supported the assignment (Figs. S1 and S2, Supporting Information).

RROP of Vinylcyclopropanes 1

The polymerizations of vinylcyclopropanes **1a–1f** were performed with azobisisobutyronitrile (AIBN) as an initiator (Scheme 3, Table 1). The vinylcyclopropanes **1b–1f** derived from L-amino acids were used as epimeric mixtures as obtained, because the chirality of the cyclopropane ring would be lost upon its ring-opening reaction during the polymerization to afford the polymers with no chiral centers in the backbone. The solvent was chosen from *N*,*N*-dimethylformamide (DMF) and toluene depending on the solubility of the resulting polymers **2**: The polymerizations of **1a**, **1b**, and **1f** proceeded in DMF efficiently, leading to the almost quantitative conversions of the monomers. The resulting polymers **2a**, **2b**, and **2f** were soluble in DMF. On the other hand, those of **1c**, **1d**, and **1e**, bearing bulky and highly hydrophobic branching alkyl groups, were performed in toluene. The corresponding polymers **2c**, **2d**, and **2e** were soluble in toluene but insoluble in DMF.

The structures of the polymers were analyzed with ^{1}H NMR, ^{13}C NMR, and IR. The spectra supported the polymer structures depicted in Scheme 3, that is, they were not contaminated by cyclobutane rings and had a *trans*-alkylene backbone (Fig. S3, Supporting Information). As typical examples, ^{1}H and ^{13}C NMR spectra of **2c** obtained by RROP of **1c** (Entry 3 in Table 1) are shown in Figure 4.

In the ^{1}H NMR spectrum of **2c**, signals attributable to the protons *a* and *b* on the vinylene moiety in the main chain appeared at 2.6 and 5.5 ppm, respectively. As well, in the ^{13}C NMR spectrum of **2c**, signals attributable to the carbons *a* and *b* on the vinylene moiety appeared at 52 and 130 ppm, respectively. In addition, in the IR spectrum of **2c**, an absorption corresponding to the *trans*-alkylene moiety in the backbone was observed at 996 cm^{-1}. The structures of the other polymers were also confirmed similarly.

TABLE 1 RROP of **1**

Entry	1	Solvent	Conversion of 1 (%)[a]	2	Yield (%)	M_n ($\times 10^3$)	M_w/M_n
1	**1a**	DMF	97	**2a**[c]	49	20[d]	3.9[d]
2	**1b**	DMF	>99	**2b**[c]	66	22[d]	2.4[d]
3	**1c**	Toluene	92	**2c**[b]	53	21[e]	1.9[e]
4	**1d**	Toluene	86	**2d**[b]	45	15[e]	1.6[e]
5	**1e**	Toluene	87	**2e**[b]	71	17[e]	1.9[e]
6	**1f**	DMF	>99	**2f**[c]	52	31[d]	2.1[d]

[a] Determined by calculating the ratio between vinyl moiety and methoxy moiety of ^{1}H NMR.
[b] Isolated as insoluble parts in a mixture of diethyl ether and hexane (1:3).
[c] Isolated as insoluble parts in diethyl ether.
[d] Estimated by SEC (calibrated by polystyrene standards, eluted with DMF containing 10 mM LiBr).
[e] Estimated by SEC (calibrated by polystyrene standards, eluted with chloroform).

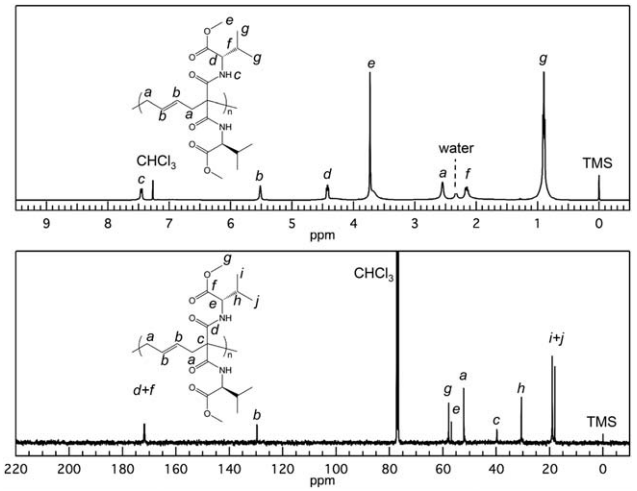


FIGURE 4 ^{1}H and ^{13}C NMR spectra of **2c** in $CDCl_3$.

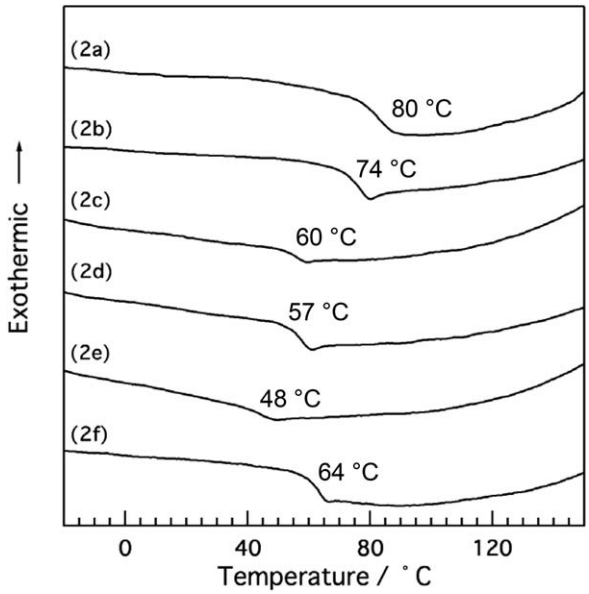


FIGURE 5 DSC thermograms of polymers **2** along with their glass transition temperatures.

Properties of Polymers 2

The resulting polymers were subjected to thermogravimetric analysis (TGA) to evaluate their thermal stability. The thermograms are shown in Figure S4, Supporting Information. For all the polymers, the temperatures of 5% weight loss by thermal degradation (T_{d5}) were higher than 300 °C (Table 2).

The glass transition temperatures (T_g) of the polymers were determined by differential scanning calorimetry (DSC) in a dynamic mode with heating rate of 10 °C/min. The polymers were heated up to 200 °C, cooled to −110 °C, and then analyzed with DSC. The resulting thermograms are shown in Figure 5. The T_g values decreased as the bulkiness of the amino acid-derived substituent increased, implying that the bulky substituents in the side chains hindered intermolecular hydrogen bonding.[24,25] The relatively high T_g of **2f** would be attributable to the rigidity of the phenyl group.

For investigating the presence and degree of hydrogen bonding in the resulting polymers **2**, their films were prepared and analyzed by IR with focusing on the absorptions attributable to the amide NH in the polymers (Fig. 6). Each of the polymers were fabricated into two films by two different processes: (1) One film (film A) was prepared by casting a polymer from its chloroform solution on the ATR prism of the IR instrument with rapid evaporation of chloroform within 1 min, and was analyzed with IR immediately. (2) The other one (film B) was prepared by casting the same solution on a Teflon petri dish with slow evaporation of chloroform taking 24 h in an incubating chamber, and then was analyzed with IR.

In the IR spectrum of film A of **2a** [Fig. 6(a), in a solid line], the amide NH absorption appeared at 3351 cm^{-1}. On the other hand, in the IR spectrum of film B of **2a** [Fig. 6(a)], in a dotted line), the amide NH absorption appeared at 3337 cm^{-1}. The difference in wavenumber indicated that the degree of hydrogen bonding in film A was less than that in film B, that is, the rapid evaporation of chloroform led to the formation of a polymer film with insufficiently grown hydrogen bonding, while the slow evaporation of chloroform permitted more efficient growth of hydrogen bonding. A similar red shift of the amide NH absorption raised by the slow evaporation was also observed for **2b**. In addition, in the IR spectrum of **2b**, the absorption at 1665 cm^{-1} attributable to the amide carbonyl stretching slightly red-shifted with accompanying a newly appeared shoulder in the red side (Fig. S5, Supporting Information), supporting the formation of hydrogen bond between amide NH and amide carbonyl moieties.

On the other hand, such clear red shifts were not observed in the IR spectra of films of **2c**, **2d**, and **2e**, regardless of film fabrication process, implying that hydrogen bonding in these polymers was sterically hindered by the bulkier substituents such as branched alkyls and benzyl in the amino acid-derived moieties [Fig. 6(c, d, and e)].

TABLE 2 Thermal properties of 2

Entry	2	T_{d5} (°C)[a]	T_g (°C)[b]
1	**2a**	300	80
2	**2b**	305	74
3	**2c**	323	60
4	**2d**	310	57
5	**2e**	323	48
6	**2f**	310	64

[a] Determined by TGA.
[b] Determined by DSC.

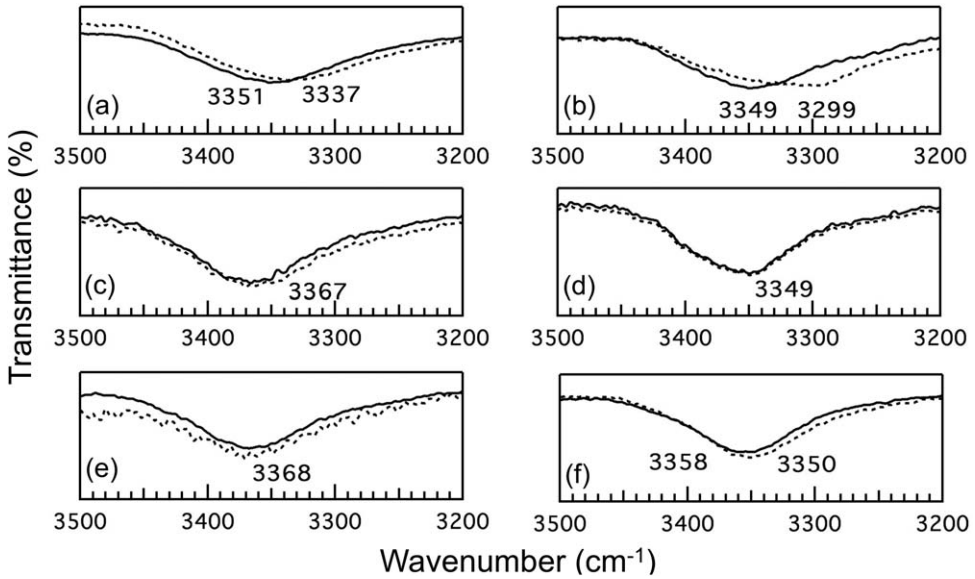


FIGURE 6 Expanded IR spectra of **2a** (a), **2b** (b), **2c** (c), **2d** (d), **2e** (e), and **2f** (f) in a range from 3200 to 3500 cm^{-1}. Solid lines indicate the IR spectra of thin films prepared on cell plate by casting from chloroform and evaporated in one minute. Dotted lines indicate the IR spectra of films prepared by casting from chloroform in an incubating chamber for 24 hours.

CONCLUSION

A series of vinylcyclopropanes bearing amino acid-derived moieties were synthesized and their radical ring-opening polymerizations (RROPs) were performed. The polymerizations proceeded efficiently to afford the corresponding polymers, of which side chains inherited the amino acid-derived moieties from the monomers. The NMR analyses of the polymers confirmed the well-defined structures of the main chains and side chains. This study using L-amino acid-derived vinylcyclopropanes has opened up possibilities of RROP as a new efficient and reliable approach to optical polymers, which are expected as new functional materials for chiral recognition, chiral discrimination, and chiral catalysis.

EXPERIMENTAL

Instruments

^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 or a solvent signal as an internal standard. IR spectra were recorded on Thermo Scientific Nicolet iS10 spectrometer equipped with a Smart iTR Sampling Accessory using attenuated total reflection (ATR) method. For the estimation of number average molecular weight (M_n) and weight average molecular weight (M_w) of the synthesized polymers, size-exclusion chromatography (SEC) was performed on a TOSOH HLC-8220 system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molecular weight); super-AW4000 (6 μm, $> 4 \times 10^5$), super-AW3000 (4 μm, $> 6 \times 10^4$), and super-AW2500 (4 μm, $> 2 \times 10^3$)] and refractive index and ultraviolet detectors. The system was operated at 40 °C using 10 mM LiBr in DMF as the eluent, at a flow rate of 0.5 mL/min. Polystyrene standards were used for calibration. The SEC using chloroform as eluent was also performed on Tosoh TSKgel SuperHM-H column (6.0 mm $\varphi \times 15$ cm, 3 and 5 μm bead sizes) at a flow rate of 0.5 mL/min at 40 °C. High-resolution mass spectra (HRMS) were obtained on a JEOL JMN-700 spectrometer using electron impact (EI) ionization mode. DSC was carried out using Seiko Instrument DSC-6200R in an aluminum pan at a heating rate 10 °C/min under a nitrogen flow of 50 mL/min. TGA was performed on a Seiko Instrument TG-DTA 6200 using an aluminum pan under nitrogen flow of 100 mL/min at a heating rate of 10 °C/min.

Chemicals

L-Amino acids, sodium hydroxide, NaH (60% dispersion in mineral oil), diethylmalonate, thionyl chloride, HOBt monohydrate, DCC, and all solvents were purchased from Wako Pure Chemical Industry (Osaka, Japan). *N*,*N*-Diisopropylethylamine, 1,4-dibromo-2-butene, and sodium hydrate were purchased from Tokyo Chemical Industry (Tokyo Japan). Tetrahydrofurane (THF), toluene, and DMF were distilled prior to use. Other solvents and reagents were used as received.

Synthesis

Synthesis of Vinylcyclopropanes 1

Typical procedure

To a solution of DCAVCP (989 mg, 6.34 mmol), which was synthesize by previously reported method,[23] in DMF (15 mL), a solution of glycine methyl ester hydrochloride (1.64 g, 11.8 mmol) and DIPEA (2.1 mL, 12.1) in DMF (25 mL) was added. The resulting mixture was cooled to 0 °C, then DCC (2.57 g, 13.4 mmol) and HOBt monohydrate (1.74 g, 12.9 mmol) were added to the mixture. After stirring the mixture at room temperature for 24 h, 2% hydrochloric acid was added and the resulting precipitate was removed by filtration. The filtrate was diluted with chloroform,

washed by sat. $NaHCO_3$ aq., and brine. The organic layer was dried over Na_2SO_4, flittered, and evaporated. The residue was fractionated by flash silica-gel column chromatography (eluent: ethyl acetate and hexane), and the fraction containing **1a** were collected, evaporated, and dried under vacuum to obtain **1a** (1.19 g, 3.99 mmol, 63%): ^{1}H NMR ($CDCl_3$): δ 7.87 (1H, br t, $J = 6.0$ Hz, NH *anti* to vinyl), 7.16 (1H, br t, $J = 6.0$ Hz, NH *syn* to vinyl), 5.53–5.44 (1H, m, C<u>H</u>=CH_2), 5.31 (1H, d, $J = 15.6$ Hz, C=C<u>H</u> (*trans*)), 5.14 (1H, d, $J = 7.8$ Hz, C=C<u>H</u> (*cis*)), 4.25 and 4.15 (1H + 1H, dd, $J = 6.4$, 18.4 Hz, N—C<u>H</u> × 2), 3.96 and 3.89 (1H + 1H, dd, $J = 5.2$, 18.4 Hz, N—C<u>H</u> × 2), 3.77 and 3.75 (3H + 3H, s, OCH_3 × 2), 2.48–242 (1H, m, C=C—C<u>H</u> × 2), 1.76 (1H, dd, $J = 6.4$, 18.0 Hz, C<u>H</u> *trans* to vinyl), 1.61 (1H, dd, $J = 5.2$, 18.0 Hz, C<u>H</u> *cis* to vinyl); HRMS (EI): found m/z 298.1165, calcd. for $C_{15}H_{22}N_2O_6$; M^+: 298.1165.

1b was Synthesized by Previously Reported Method.[23]

According to the typical procedure, DCAVCP and L-valine methyl ester hydrochloride were condensed to obtain **1c** (2.47 g, 6.47 mmol, 68%): ^{1}H NMR ($CDCl_3$): δ 7.66 and 7.53 (1H + 1H, d, $J = 8.0$ Hz, NH *anti* to vinyl × 2), 7.00 and 6.80 (1H + 1H, d, $J = 7.6$, NH *syn* to vinyl × 2), 5.63-5.54, 5.47-5.39 (1H, m, C<u>H</u>=CH_2 × 2), 5.35-5.28 (2H, m, C=C<u>H</u> (*trans*) × 2), 5.20-5.11 (2H, m, C=C<u>H</u> (*cis*) × 2), 4.53-4.45 (4H, m, N—C<u>H</u> × 4), 3.76, 3.74_9, 3.74_5, 3.73 (each 3H, s, OCH_3 × 4), 2.51-2.45, 2.36-2.30 (1H + 1H, m, C=C—C<u>H</u> × 2), 2.28-2.15 (4H, m, C<u>H</u>$(CH_3)_2$ × 4), 1.83, 1.70 (1H + 1H, dd, $J = 5.2$, 9.2 Hz, C<u>H</u> (*cis* to vinyl) × 2), 1.65, 1.55 (1H + 1H, dd, $J = 5.2$, 6.8 Hz, C<u>H</u> (*trans* to vinyl)), 0.983-0.918 (12H, m, CH($C\underline{H}_3$)$_2$ × 2): HRMS (EI): found m/z 382.2105, calcd. for $C_{15}H_{22}N_2O_6$; M^+: 382.2104.

According to the typical procedure, DCAVCP and L-leucine methyl ester hydrochloride were condensed to obtain **1d** (2.34 g, 5.71 mmol, 85%): ^{1}H NMR ($CDCl_3$): δ 7.87, 7.40 (1H + 1H, d, $J = 7.2$ Hz, NH *anti* to vinyl × 2), 7.04, 7.01 (1H + 1H, d, $J = 7.2$, NH *syn* to vinyl × 2), 5.62-5.53 (1H, m, C<u>H</u>=CH_2), 5.39-5.26 (3H, m, C<u>H</u>=CH_2 + CH=C<u>H</u> (*trans*) × 2), 5.16-5.07 (2H, m, CH=C<u>H</u> (*cis*) × 2), 4.62-4.52 (4H, m, N—C<u>H</u> × 4), 3.76, 3.75, 3.74, 3.73 (each 3H, s, OCH_3 × 4), 2.61-2.55, 2.35-2.29 (1H + 1H, m, C=C—C<u>H</u> × 2), 1.80-1.60 (15H, m, C=C—CH—C<u>H</u> × 3 + $C\underline{H}_2C\underline{H}(CH_3)_2$ × 4), 1.48 (1H, dd, $J = 5.2$, 7.2 Hz, C<u>H</u> (*trans* to vinyl)), 0.96-0.90 (12H, m, CH($C\underline{H}_3$)$_2$ × 2); HRMS (EI): found m/z 410.2416, calcd. for $C_{15}H_{22}N_2O_6$; M^+: 410.2417.

According to the typical procedure, DCAVCP and L-isoleucine methyl ester hydrochloride were condensed to obtain **1e** (2.80 g, 6.83 mmol, 87%): ^{1}H NMR ($CDCl_3$): δ 7.70, 7.53 (1H + 1H, d, $J = 7.6$ Hz, NH *anti* to vinyl × 2), 7.00, 6.84 (1H + 1H, d, $J = 8.0$ Hz, NH *syn* to vinyl × 2), 5.56-5.51 (1H, m, C<u>H</u>=CH_2), 5.46-5.37 (1H, m, C<u>H</u>=CH_2), 5.34-5.27 (2H, m, C=C<u>H</u> (*trans*) × 2), 5.19-5.10 (2H, m, CH=C<u>H</u> (*cis*) × 2), 4.57-4.46 (4H, m, N—C<u>H</u> × 4), 3.76, 3.74, 3.74, 3.73 (each 3H, s, OCH_3 × 4), 2.49–242, 2.35-2.29 (1H + 1H, m, C=C—C<u>H</u> × 2), 2.01-1.86 (4H, m, C<u>H</u>$(CH_3)CH_2$ × 4) 1.81, 1.69 (1H + 1H, dd, $J = 5.2$, 8.8 Hz, C<u>H</u> (*cis* to vinyl) × 2) 1.62 and 1.53 (1H, dd, $J = 4.8$, 7.6 and 5.6, 6.8 Hz, C<u>H</u> (*trans* to vinyl)), 0.95-0.81 (12H, m, CH($C\underline{H}_3$)$_2$ × 2): HRMS (EI): found m/z 410.2417, calcd. for $C_{15}H_{22}N_2O_6$; M^+: 410.2417.

According to the typical procedure, DCAVCP and L-phenylalanine methyl ester hydrochloride were condensed to obtain **1f** (1.07 g, 2.2 mmol, 60%): ^{1}H NMR ($CDCl_3$): δ 7.69, 7.40 (1H + 1H, d, $J = 8.0$ Hz, NH *anti* to vinyl × 2), 7.29-7.11 (10H, m, aromatic) 6.87, 6.81 (1H + 1H, d, $J = 7.2$, NH *syn* to vinyl × 2), 5.20-5.09, 5.02–4.99, 4.91-4.88 (4H + 1H + 1H, m, C<u>H</u>=$C\underline{H}_2$ × 2), 4.89-4.73 (4H, m, N-C<u>H</u> × 4), 3.76, 3.73, 3.70, 3.69 (each 3H, s, OCH_3 × 4), 3.23-3.11, 3.07-2.96 (4H + 4H, m, $C\underline{H}_2$-phenyl), 2.35-2.30, 2.11-2.05 (1H + 1H, m, C=C—C<u>H</u> × 2), 1.69, 1.49, 1.31 (1H + 2H + 1H, m, C<u>H</u> (*cis* to vinyl) × 2 + C<u>H</u> (*trans* to vinyl) × 2). HRMS (EI): found m/z 478.2105, calcd. for $C_{27}H_{30}N_2O_6$; M^+: 478.2104.

Radical ROP of Vinylcyclopropanes 1

Typical procedure

Vinylcyclopropane **1a** (150.0 mg, 503 μmol) and AIBN (2.4 mg, 15.1 μmol, 3 mol% to **1a**) were dissolved in 0.5 μL of distilled DMF. The solution was degassed by three freeze-thaw cycles, sealed, and heated at 60 °C. After 20 h, the solution was diluted with chloroform (5 mL) and added to diethyl ether (300 mL). The resulting white precipitates were collected by filtration with suction and dried under vacuum to obtain polymer **2a** (101.1 mg, 67%): ^{1}H NMR ($CDCl_3$): δ 7.65 (2H, brs, NH × 2), 5.54 (2H, brs, C<u>H</u>=C<u>H</u>), 3.99 (4H, d, $J = 4.4$ Hz, N—CH_2 × 2), 3.72 (6H, brs, OCH_3 × 2), 2.56 (4H, brs, $C\underline{H}_2$—CH=CH—$C\underline{H}_2$); ^{13}C NMR ($CDCl_3$): δ 172.66, 170.70, 129.44, 56.81, 52.40, 41.59, 39.05; IR (ATR): ε 3351 (NH), 1742 (C=O ester), 1662 (C=O amide), 978 (C=CH *trans*).

According to the typical procedure, **1c** was polymerized in toluene to obtain polymer **2c** (285.6 mg, 53%): ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, brd, $J = 7.6$ Hz, NH × 2), 5.52 (2H, brs, C<u>H</u>=C<u>H</u>), 4.43 (2H, dd, $J = 5.2$, 7.6 Hz, N—C<u>H</u> × 2), 3.73 (6H, brs, OCH_3 × 2), 2.55 (4H, brs, $C\underline{H}_2$—CH=CH—$C\underline{H}_2$), 2.20-2.12 (2H, m, C<u>H</u>$(CH_3)_2$ × 2), 0.90 (12H, t, $J = 6.0$Hz, CH_3 × 4); ^{13}C NMR ($CDCl_3$): δ 172.01, 171.75, 129.69, 57.84, 56.81, 52.17, 39.78, 30.61, 19.05, 18.06; IR (ATR): ε 3358 (NH), 1740 (C=O ester), 1663 (C=O amide), 993 (C=CH *trans*).

According to the typical procedure, **1d** was polymerized in toluene to obtain polymer **2d** (259.3 mg, 45%): ^{1}H NMR ($CDCl_3$): δ 7.32 (2H, br d, $J = 6.8$ Hz, NH × 2), 5.51 (2H, brs, C<u>H</u>=C<u>H</u>), 4.50 (2H, br t, $J = 6.8$ Hz, N—C<u>H</u> × 2), 3.72 (6H, br s, OCH_3 × 2), 2.51 (4H, brs, $C\underline{H}_2$—CH=CH—$C\underline{H}_2$), 1.60 (6H, brs, $C\underline{H}_2C\underline{H}(CH_3)_2$ × 2), 0.92 (12H, t, $J = 4.0$Hz, CH_3 × 4); ^{13}C NMR ($CDCl_3$): δ 173.65, 171.93, 129.62, 56.98, 52.36, 51.347, 40.167, 39.57, 24.91, 22.94, 21.48; IR (ATR): ε 3349 (NH), 1740 (C=O ester), 1668 (C=O amide), 981 (C=CH *trans*).

According to the typical procedure, **1e** was polymerized in toluene to obtain polymer **2e** (639.3 mg, 71%). ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, br d, $J = 6.8$ Hz, NH × 2), 5.52 (2H, br s, C<u>H</u>=C<u>H</u>), 4.47 (2H, br t, $J = 6.0$ Hz, N—C<u>H</u> × 2), 3.73 (6H,

br s, OCH_3 × 2), 2.54 (4H, br s, $\underline{CH_2}$—CH═CH—$\underline{CH_2}$), 1.88 (2H, br s, NCHC$\underline{H}$ × 2), 1.43-1.11 (4H, m, ($\underline{CH_2}CH_3$) × 2) 0.92-0.86 (12H, m, J = 4.0Hz, CH_3 × 4); ^{13}C NMR ($CDCl_3$): 171.98, 171.58, 129.76, 57.07, 56.72, 52.11, 39.75, 37.20, 25.33, 15.58, 11.58; IR (ATR): ε 3368 (NH), 1739 (C═O ester), 1672 (C═O amide), 985 (C═CH *trans*).

According to the typical procedure, **1f** was polymerized in DMF to obtain polymer **2f** (124.7 mg, 52%): ^{1}H NMR ($CDCl_3$): δ 7.35 (2H, br d, J = 6.4 Hz, NH × 2), 7.25-7.06 (20H, m, aromatic), 5.16 (2H, brs, C$\underline{H}$═C$\underline{H}$), 4.47 (2H, brt, J = 6.4, 6.4 Hz, N—CH × 2), 3.62 (6H, brs, $\underline{OCH_3}$ × 2), 3.09-2.96 (4H, m, CH_2-phenyl × 2) 2.24 (4H, brs, $\underline{CH_2}$—CH═CH-C$\underline{H_2}$); ^{13}C NMR ($CDCl_3$): δ 171.89, 171.45, 136.18, 129.11, 128.56, 128.31, 127.07, 56.33, 54.02, 52.29, 39.18, 37.41; IR (ATR): ε 3358 (NH), 1740 (C═O ester), 1663 (C═O amide), 983 (C═CH *trans*).

ACKNOWLEDGMENTS

This work was financially supported by JSR Corporation. The high-resolution mass spectrometry (HRMS) experiment was performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

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