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Synthesis and properties of optically active substituted polyacetylenes having carboxyl and/or amino groups

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Abstract

Polyacetylenes having carboxyl and/or amino groups in the side chain were synthesized by the polymerization of *N*-(2-propynyloxycarbonyl)-L-alanine (**1**) and L-alanine *N*-propargylamide (**2**) catalyzed with a rhodium cation complex. Poly($\mathbf{1}_{0.5}$-*co*-$\mathbf{2}_{0.5}$) exhibited a larger CD signal than the homopolymers. The polymer mixtures obtained by the polymerization of **1** in the presence of poly(**2**), and those obtained by the polymerization of **2** in the presence of poly(**1**) showed specific rotations larger than calculated. The polymerization of propargylamine in the presence of poly(**1**) did not exhibit significant effect, while the polymer mixtures obtained by the polymerization of propiolic acid in the presence of poly(**2**) exhibited $[\alpha]_D$ of positive sign, although poly(**2**) alone exhibited $[\alpha]_D$ of negative sign.

Keywords: Polyacetylene; Amino group; Carboxyl group

1. Introduction

Amino acids are constituents of proteins, typical biological polymers, and are not only biologically important but also are useful substances for chiral auxiliaries and building blocks in organic synthesis [1]. Amino acid-based synthetic polymers are also expected to show biocompatibility and biodegradability similarly to polypeptides [2]. On the other hand, polyacetylenes possess alternating double bonds in the main chain, which endows polyacetylenes with electrical conductivity, paramagnetism, energy migration and transfer, chemical reactivity and complex formation, gas permeability, etc. [3]. It is expected that amino acid-containing polyacetylenes will combine these characteristics together and lead to the development of new functions. We have recently reported the synthesis of an alanine-based polyacetylene by the polymerization of an alanine-derived *N*-propargylamide [*N*-(*tert*-butoxycarbonyl)-L-alanine *N*′-propargylamide in Scheme 1] catalyzed by an Rh^+ complex [4]. The formed polymer takes a helical conformation in a chloroform solution. Hydrogen bonding involving N–H linkage plays an important role in stabilizing the helical conformation. Tang and coworkers have reported the synthesis of poly(phenylacetylene)s carrying amino acid pendants [5].

Meanwhile, template polymerization is a new field in polymer synthesis but common practice in biosynthesis, since DNA is the most popular template, on which proteins are built by living species [6]. If we polymerize amino acid-derived acetylene monomers having non-protected amino and/or carboxyl groups, we can obtain novel optically active environmentally friendly polymers, which may be applicable to template polymerization. The present article deals with polymerization of amino acid-derived acetylene monomers having carboxyl and amino groups, copolymerization of the monomers, polymerization of the amino group-carrying monomer in the presence of the carboxyl group-carrying polymer, and polymerization of the carboxyl group-carrying monomer in the presence of the amino group-carrying polymer, along with examination of template effect on the polymerization.

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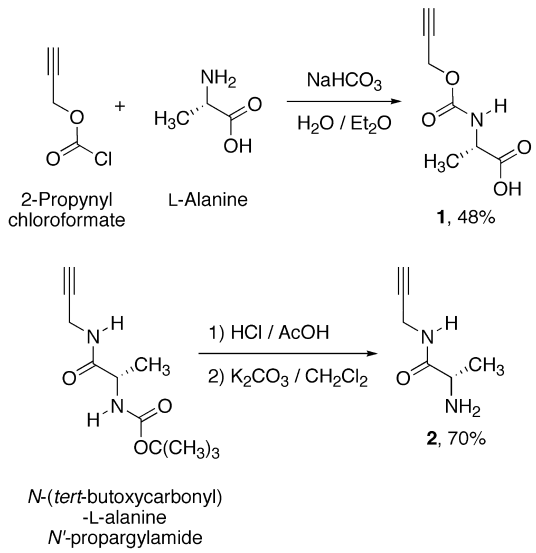


Scheme 1.

2. Experimental

2.1. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was done at the Kyoto University Elemental Analysis Center. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-100 digital polarimeter with a sodium lamp as a light source. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using THF as an eluent at a flow rate of 1.0 ml/min, calibrated by polystyrene standards at 40 °C. Otherwise, they were determined by GPC on a Tosoh 8020 instrument with a TSH-gel Alpha 3000 column using a 10 mM LiBr solution in *N*,*N*-dimethylformamide (DMF) at a flow rate of 1.0 ml/min, calibrated by polystyrene standards at 40 °C. CD spectra were measured in a quartz cell (thickness: 1 cm) at room temperature using a JASCO J-800 spectropolarimeter.

2.2. Materials

All the reagents in monomer synthesis were used as purchased without purification. (nbd)Rh^{+}[η^{6}-C_6H_5B-$(C_6H_5)_3$] (nbd = 2,5-norbornadiene) [7], 2-propynyl chloroformate [8], *N*-(*tert*-butoxycarbonyl)-L-alanine *N*′-propargylamide [4] were synthesized according to the literature. THF, MeOH, and CH_2Cl_2 were distilled by the standard procedures.

2.3. Monomer synthesis

2.3.1. *N*-(2-Propynyloxycarbonyl)-L-alanine (**1**)

A solution of 2-propynyl chloroformate (1.58 g, 13 mmol) in ether (60 ml) was slowly added to a solution of L-alanine (1.83 g, 25 mmol) and $NaHCO_3$ (4.46 g, 53 mmol) in water (30 ml) at room temperature. Two hours after the addition was completed, 2-propynyl chloroformate (1.58 g, 13 mmol) and $NaHCO_3$ (2.23 g, 27 mmol) were added to the reaction mixture, and the resulting mixture was stirred for 3 h. It was washed with ether, and 6 M HCl (20 ml) was added to acidify the mixture. It was extracted with ethyl acetate (60 ml), and the organic layer was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to obtain the product. Yield 48%. $[\alpha]_D = -6.1°$ ($c = 0.1$ g/dl, MeOH at r.t.). IR (NaCl, neat): 3284 ($\nu_{\equiv C-H,\ -OH}$), 2118 ($\nu_{C\equiv C}$), 1720 ($\nu_{C=O}$), 1535, 1253, 1075 cm^{-1}. ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.48 (d, $J = 6.8$ Hz, 3H), 2.49 (s, 1H), 4.40–4.43 (m, 1H), 4.70 (s, 2H), 5.43 (s, 1H), 6.23 (s, 1H) ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 18.7 (–CH_3), 49.2 (–CH_2–), 52.8 (–CH–), 74.9 (≡CH), 77.5 (–*C*≡CH), 154.9 (–OCONH–), 177.1 (–CO_2H). Anal. Calcd for $C_7H_9O_4N$: C, 49.12; H, 5.30; N, 8.18. Found: C, 48.45; H, 5.60; N, 8.22.

2.3.2. L-Alanine *N*-propargylamide (**2**)

1 M HCl (125 ml) and acetic acid (50 ml) were added to *N*-(*tert*-butoxycarbonyl)-L-alanine *N*′-propargylamide (2.26 g, 10 mmol), and the resulting mixture was stirred at room temperature for 2 h. It was concentrated by rotary evaporation. CH_2Cl_2 (25 ml) and K_2CO_3 (3.45 g, 25 mmol) were added to the resulting mass, and the mixture was filtered. The filtrate was concentrated to obtain the product. Yield 70%. $[\alpha]_D = +5.2°$ ($c = 0.1$ g/dl, MeOH at r.t.). IR (NaCl, neat): 3300, 2972, 2120 ($\nu_{C\equiv C}$), 1658 ($\nu_{C=O}$), 1260, 670 cm^{-1}, ^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 1.33 (d, $J = 6.8$ Hz, 3H), 1.63 (s, 2H), 2.26 (s, 1H), 3.49–3.54 (m, 1H), 4.05 (s, 2H), 7.68 (s, 1H), ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 21.7 (–CH_3), 28.9 (–CH_2–), 50.7 (–CH–), 71.4 (≡CH), 79.9 (–*C*≡CH), 175.7 (C=O). Anal. Calcd for $C_6H_{10}ON_2$: C, 57.12; H, 7.99; N, 22.21. Found. C, 57.41; H, 8.05; N, 22.41.

2.4. Polymerization

Homo and copolymerizations. All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. (nbd)Rh^{+}[η^{6}-$C_6H_5B^{-}(C_6H_5)_3$] (25.7 mg, 0.05 mmol) was added to a solution of monomer (1 mmol), and the resulting mixture was vigorously stirred. It was kept in a water bath at 30 °C for 24 h. The resulting mixture was poured into *n*-hexane or ether (200 ml) to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A), and dried under reduced pressure.

Table 1
Homo and copolymerizations of **1** and **2**

Run	Monomer feed ratio **1**:**2**	Solvent (mol/l)	$[M]_0$ (%)	Yield[a]	M_n [b]	M_w/M_n (°)[b]	$[\alpha]_D$[c]
1	100:0	THF	1.0	97	1400	1.43	−16.2
2	100:0	THF[d]	1.0	99	4800	1.32	–[e]
3	100:0	MeOH	0.1	48	–[f]	–[f]	−23.8
4	75:25	MeOH	0.1	70	–[g]	–[g]	−72.7
5	50:50	MeOH	0.1	92	–[g]	–[g]	−93.9
6	25:75	MeOH	0.1	28	–[g]	–[g]	−48.3
7	0:100	MeOH	0.1	92	–[h]	–[h]	−11.9
8	0:100	CH_2Cl_2	1.0	99	–[g]	–[g]	–[e]
9	0:100	CH_2Cl_2	0.1	59	–[g]	–[g]	–[e]

30 °C, 24 h, $[Cat.]/[M]_0 = 0.05$.

[a] When THF and CH_2Cl_2 were used as the solvent, the polymer was isolated by precipitation in *n*-hexane (runs 1, 2, 8, and 9). When MeOH was used as the solvent, it was isolated by precipitation in ether (runs 3–7).

[b] Estimated by GPC calibrated by polystyrene standard samples. Eluent: THF (runs 1 and 2), DMF (runs 3 and 7).

[c] Measured by polarimetry in MeOH, $c = 0.11–0.09$ g/dl at r.t.

[d] Diethylamine (1.5 equiv. to **1**) was added.

[e] Not determined.

[f] The GPC exhibited three peaks; peak 1 $M_n = 2000$, $M_w/M_n = 1.13$ (9%), peak 2 $M_n = 200$, $M_w/M_n = 1.48$ (71%), peak 3 $M_n = 100$, $M_w/M_n = 1.00$ (20%).

[g] Polymer was insoluble in THF and DMF.

[h] The GPC exhibited three peaks; peak 1: $M_n = 3100$, $M_w/M_n = 1.20$ (16%), peak 2: $M_n = 160$, $M_w/M_n = 1.32$ (73%), peak 3: $M_n = 100$, $M_w/M_n = 1.00$ (11%).

Polymerization in the presence of another polymer. The Rh catalyst was added to a solution of a monomer and poly(**1**) or poly(**2**) in MeOH. Otherwise, it was carried out in a manner similar to the homo and copolymerizations. The polymer formed was obtained as a mixture with the poly(**1**) or poly(**2**) fed beforehand.

2.5. Spectroscopic data of polymers

2.5.1. Poly(*1*)

^{1}H NMR (400 MHz, δ in ppm, DMSO-d_6): 1.3 (broad s, 3H), 4.0 (broad s, 2H), 4.5 (broad s, 1H), 5.5–6.5 (broad, 1H), 7.0–7.5 (broad, 1H), 12.5 (broad s, 1H).

2.5.2. Poly(*2*)

^{1}H NMR (400 MHz, δ in ppm, DMSO-d_6): 1.4 (broad s, 3H), 3.4–4.5 (broad, 6H), 7.0–7.5 (broad, 1H).

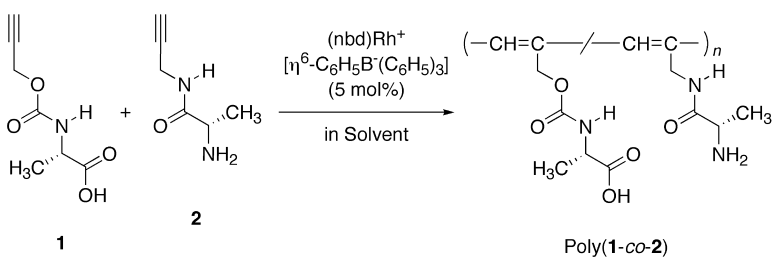
3. Results and discussion

3.1. Monomer synthesis

Scheme 1 illustrates the synthetic procedures for the novel alanine-based acetylene monomers **1** and **2**. The acidic monomer **1** was synthesized by *N*-acylation of L-alanine with 2-propynyl chloroformate in 48% yield. The basic monomer **2** was synthesized by HCl/AcOH-deprotection of BOC group of the previously reported alanine-based *N*-propargylamide, followed by neutralization of the corresponding ammonium salt using alkali in 70% yield. The monomers were identified by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis.

3.2. Polymerization

Table 1 summarizes the conditions and results of the homo- and copolymerizations of **1** and **2** catalyzed by 5 mol% of $(nbd)Rh^+[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ in THF, MeOH, and CH_2Cl_2 at 30 °C for 24 h (Scheme 2). When the polymerization of **1**



Scheme 2.

Table 2
Solubility of poly(**1**), poly(**2**), and poly($\mathbf{1}_{0.5}$-*co*-$\mathbf{2}_{0.5}$)

	Hexane	$CHCl_3$	CH_2Cl_2	THF	DMF	MeOH	MeOH/1 M HCl = 1:1 (volume ratio)	H_2O
Poly(**1**)	−	−	−	[a]	+	+	+	±
Poly(**2**)	−	−	−	−	+	±	+	±
Poly($\mathbf{1}_{0.5}$-*co*-$\mathbf{2}_{0.5}$)	−	−	−	−	−	±	+	±

Sample 1 mg/solvent 1 ml, +: soluble, ±: partly soluble, −: insoluble. Poly(**1**), poly(**2**), poly($\mathbf{1}_{0.5}$-*co*-$\mathbf{2}_{0.5}$): runs 3, 7, and 5 in Table 1, respectively.
[a] The poly(**1**) obtained by the polymerization in THF (runs 1 and 2 in Table 1) was soluble in THF, while the poly(**1**) obtained by the polymerization in MeOH (run 3 in Table 1) was insoluble in THF.

was carried out in THF, the polymer formed was completely soluble in THF (runs 1 and 2). On the other hand, when it was done in MeOH, the polymer formed was partly insoluble in THF (run 3). Acetic acid is used as a quencher of polymerization of phenylacetylenes with organorhodium complexes [9]. It is therefore noteworthy that the carboxyl group-containing monomer **1** underwent polymerization, although the degree of polymerization was low. Considering from the molecular weights of the monomer **1**, it is assumed that the degree of polymerization is ca. 30 in the case of run 2. The degree of deactivation of the Rh catalyst by the carboxyl group might be low compared to acetic acid, presumably due to the substituent. The addition of diethylamine was effective to increase the molecular weight of the polymer (run 2). The copolymerization of **1** and **2** was conducted at a relatively small initial monomer concentration ($[M]_0 = 0.1$ M), because the solubility of both monomers was not so high. The molecular weights of the copolymers could not be estimated by GPC, because they were insoluble in $CHCl_3$, THF, and DMF. The homopolymers obtained by the polymerization in MeOH exhibited multimodal GPC traces, and the molecular weights were low (runs 3 and 7). It is interesting that the copolymers (runs 4–6) exhibited specific rotations larger than those of the homopolymers (runs 3 and 7). When the polymerization of **2** was carried out in CH_2Cl_2, the polymer formed was insoluble in THF and DMF (runs 8 and 9).

Table 2 summarizes the solubility of the homopolymers and copolymer of **1** and **2** (copolymerization feed ratio = 1:1). The polymers were poorly soluble in organic solvents, while soluble in a mixed solvent of MeOH and 1 M HCl.

We next examined the polymerization of basic monomer **2** in the presence of acidic poly(**1**). Polymer mixtures with η_{inh} ranging from 0.051 to 0.071 were obtained in 48–94% yields as summarized in Table 3 [10]. The low viscosities (molecular weights) of the polymer mixtures should be due to the deactivation of the Rh catalyst by the carboxyl groups of poly(**1**). It is noteworthy that the polymer mixtures exhibited specific rotations larger than those calculated from the data of the homopolymers. Interaction between monomer **2** and poly(**1**) might influence the polymerization of **2** resulting in this phenomenon. This is supported by the fact that the $[\alpha]_D$ of an equivalent mixture of poly(**1**) and poly(**2**) was −19.2°, which is smaller than the data of run 5 in Table 3 (−36.5°), and almost the same as that of theoretical value (−18.8°), which was calculated assuming that the specific rotations of poly(**1**) and poly(**2**) are not affected each other. The η_{inh} of the equivalent mixture of both polymers was 0.129 dl/g.

Table 4 summarizes the results of the polymerization of

Table 3
Polymerization of **2** in the presence of poly(**1**)

Run	[Poly(**1**)]/[**2**]$_0$ (%)[a]	Yield (%)[b]	η_{inh} (dl/g)[c]	$[\alpha]_D$ (°)[d]	Theoretical value of $[\alpha]_D$ (°)[e]
1	0	92	0.302	−11.9	−11.9
2	25	53	–[f]	−26.8	−14.9
3	50	48	–[f]	−33.0	−16.7
4	75	85	0.063	−25.2	−17.9
5	100	91	0.051	−36.5	−18.8
6	125	94	0.071	−25.5	−19.4

30 °C, 24 h, [Cat.] = 5 mM, $[M]_0 = 0.10$ M in MeOH.
[a] Ratio between the repeating unit of poly(**1**) and **2** in feed. Poly(**1**) was obtained by the polymerization of run 3 in Table 1.
[b] Ether-insoluble part, total of poly(**1**) and poly(**2**).
[c] Measured as a mixture of poly(**1**) and poly(**2**) by a viscometer in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.50$ g/dl, at r.t.
[d] Measured as a mixture of poly(**1**) and poly(**2**) by polarimetry in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.11 - 0.09$ g/dl, at r.t.
[e] Calculated by the following equation. $[\mathbf{2}]_0 \times [\alpha]_{D\ poly(\mathbf{2})}/([\text{poly}(\mathbf{1})] + [\mathbf{2}]_0) + [\text{poly}(\mathbf{1})] \times [\alpha]_{D\ poly(\mathbf{1})}/([\text{poly}(\mathbf{1})] + [\mathbf{2}]_0)$.
[f] Not determined.

Table 4
Polymerization of **1** in the presence of poly(**2**)

Run	[Poly(**2**)]/[**1**]$_0$ (%)[a]	Yield (%)[b]	η_{inh} (dl/g)[c]	$[\alpha]_D$ (°)[d]	Theoretical value of $[\alpha]_D$ (°)[e]
1	0	48	0.069	−23.8	−23.8
2	25	82	0.150	−28.5	−21.9
3	50	86	0.148	−34.0	−20.4
4	75	86	0.166	−29.3	−19.3
5	100	94	0.173	−35.6	−18.5
6	125	87	0.247	−30.1	−17.8

30 °C, 24 h, [Cat.] = 0.5 mM, $[M]_0 = 0.10$ M in MeOH.
[a] Ratio between the repeating unit of poly(**2**) and **1** in feed. Poly(**2**) was obtained by the polymerization of run 7 in Table 1.
[b] Ether-insoluble part, polymer mixture yield.
[c] Measured as a mixture of poly(**1**) and poly(**2**) by a viscometer in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.50$ g/dl, at r.t.
[d] Measured as a mixture of poly(**1**) and poly(**2**) by polarimetry in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.11 - 0.09$ g/dl, at r.t.
[e] Calculated by the following equation. $[\mathbf{1}]_0 \times [\alpha]_{D\ (poly(\mathbf{1})}/([\text{poly}(\mathbf{2})] + [\mathbf{1}]_0) + [\text{poly}(\mathbf{2})] \times [\alpha]_{D\ (poly(\mathbf{2})}/([\text{poly}(\mathbf{2})] + [\mathbf{1}]_0)$.

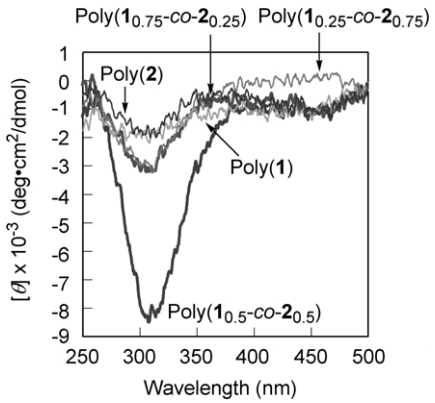
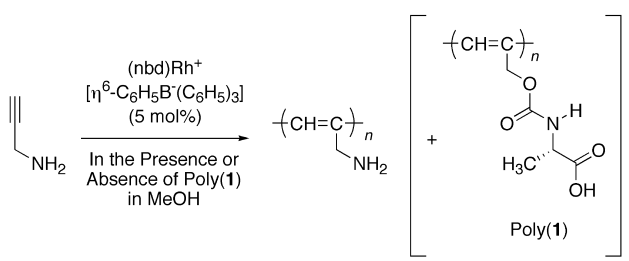


Fig. 1. CD spectra of poly(**1**), poly(**1**$_{0.75}$-*co*-**2**$_{0.25}$), poly(**1**$_{0.5}$-*co*-**2**$_{0.5}$), poly(**1**$_{0.25}$-*co*-**2**$_{0.75}$), and poly(**2**) measured in MeOH, $c = 10^{-4}$ g/dl at r. t. Samples: runs 3–7 in Table 1.

acidic monomer **1** in the presence of basic poly(**2**). Polymer mixtures with η_{inh} ranging from 0.069 to 0.247 were obtained in 48–94% yields. The viscosity of the polymer mixture increased as the ratio of poly(**2**) increased. This is reasonable because the presence of amines enhances the polymerization efficiency of acetylene monomers having carboxyl group [11]. The polymer mixtures exhibited specific rotations larger than those calculated from the data of the homopolymers in a manner similar to the case of Table 3. This is also the case that shows the presence of interaction between the monomer and the polymer fed beforehand.

Fig. 1 depicts the CD spectra of poly(**1**), poly(**2**), and poly(**1**-*co*-**2**)s. At this low polymer concentration ($c = 1 \times 10^{-4}$ g/dl), the polymers were completely soluble in MeOH. It is noteworthy that poly(**1**$_{0.5}$-*co*-**2**$_{0.5}$) exhibited a CD signal at 310 nm much larger than those of the homopolymers. The copolymer may partly take some higher order structures such as helix. Alternating unit sequence may be dominant in the copolymer, because it is likely that an acidic propagating end preferably reacts with a basic monomer, and a basic propagating end prefers an acidic monomer, which may correlate with the formation of higher order structures.

We further examined the polymerization of propargylamine in the presence of poly(**1**) (Scheme 3, Table 5). The total polymer yield and viscosity increased by the presence of poly(**1**) and diethylamine. No significant effect of poly(**1**)



Scheme 3.

Table 5
Polymerization of propargylamine in the presence of poly(**1**)

Run	[Propargylamine]$_0$		Yield (%)[a]	η_{inh} (dl/g)[b]	$[\alpha]_D$ (°)[c]
	[Poly(**1**)][d]	[Diethylamine]			
1	0	0	30	–[e]	+1.2
2	1	0	74	0.038	−15.9
3	1	1	98	0.087	−19.4

30 °C, 24 h, [Cat.] = 5 mM, [M]$_0$ = 0.10 M in MeOH.
[a] Ether-insoluble part, total of poly(**1**) and poly(propargylamine).
[b] Measured as a mixture of poly(**1**) and poly(propargylamine) by a viscometer in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.50$ g/dl, at r.t.
[c] Measured as a mixture of poly(**1**) and poly(propargylamine) by polarimetry in MeOH, $c = 0.11 - 0.09$ g/dl, at r.t.
[d] Ratio between the repeating unit of poly(**1**) and propargylamine in feed. Poly(**1**) was obtained by the polymerization of run 3 in Table 1.
[e] Not determined.

fed before hand could be observed in the specific rotation of the obtained polymer mixture.

Table 6 summarizes the results of the polymerization of propiolic acid in the presence of poly(**2**) (Scheme 4), a counterpart of Table 5. The addition of diethylamine was effective to increase the viscosity of the formed polymer mixture. Poly(**2**) exhibited $[\alpha]_D$ of negative sign as shown in run 7 in Table 1, while the polymer mixture obtained by the polymerization of propiolic acid in the presence of poly(**2**) exhibited $[\alpha]_D$ of positive sign. It is considered that the interaction between the amino group of poly(**2**) and propiolic acid affected the conformation and structure of the formed polymers, resulting in this difference.

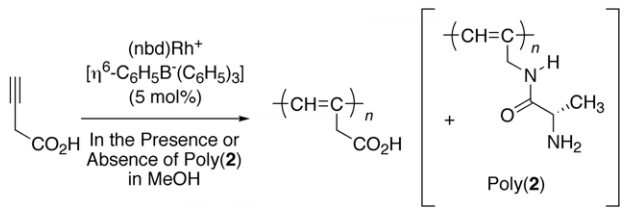
4. Summary

In this article, we demonstrated the synthesis of polyacetylenes having carboxyl and/or amino groups in the side chain. The CD signal of poly(**1**$_{0.5}$-*co*-**2**$_{0.5}$) was larger than those of the homopolymers, which suggested that the high order structure and/or unit sequence of the copolymers

Table 6
Polymerization of propiolic acid in the presence of poly(**2**)

Run	[Propiolic acid]$_0$		Yield (%)[a]	η_{inh} (dl/g)[b]	$[\alpha]_D$ (°)[c]
	[Poly(**2**)][d]	[Diethylamine]			
1	0	1	60	0.101	+2.2
2	1	0	79	0.068	+46.8
3	1	1	64	0.086	+34.5

30 °C, 24 h, [Cat.] = 5 mM, [M]$_0$ = 0.10 M in MeOH.
[a] Ether-insoluble part, total of poly(**1**) and poly(propiolic acid).
[b] Measured as a mixture of poly(**2**) and poly(propiolic acid) by a viscometer in MeOH/1 M HCl = 1/1 (volume ratio), $c = 0.50$ g/dl, at r.t.
[c] Measured as a mixture of poly(**2**) and poly(propiolic acid) by polarimetry in MeOH, $c = 0.11 - 0.09$ g/dl, at r.t.
[d] Ratio between the repeating unit of poly(**2**) and propiolic acid in feed. Poly(**2**) was obtained by the polymerization of run 7 in Table 1.



Scheme 4.

was affected by ionic interaction between the carboxyl and amino groups. When the polymerization of **1** was carried out in the presence of poly(**2**), and that of **2** was done in the presence of poly(**1**), the $[\alpha]_D$ of the resulting polymer mixtures took larger values than the theoretical ones based on the $[\alpha]_D$ of poly(**1**) and poly(**2**). This result suggests that the $[\alpha]_D$ of the formed polymers was affected by the polymers fed beforehand, probably due to ionic interaction between the carboxyl and amino groups. The polymerization of propargylamine in the presence of poly(**1**) did not exhibit significant effect, while the polymer mixtures obtained by the polymerization of propiolic acid in the presence of poly(**2**) exhibited $[\alpha]_D$ of positive sign, although poly(**2**) alone exhibited $[\alpha]_D$ of negative sign. This result indicates that the $[\alpha]_D$ of poly(**2**) was affected by poly(propiolic acid). In the future, we may develop novel template polymerization system based on the present study by designing amino acid-containing polymers having carboxyl or amino group, which are capable to take clear helical structure.

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[10] In this experiment, poly(**1**) obtained by the polymerization in MeOH (run 3 in Table 1) was employed to unify the solvent for preparation of poly(**1**) and the polymerization of **2** in the presence poly(**1**) along with to achieve homogeneous polymerization, although the poly(**1**) contained low-molecular weight fractions.

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