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Stabilization of higher-order structure of poly(phenyleneethynylene)s by metathesis polymerization at the side chains

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ABSTRACT

Novel poly(*m*-phenyleneethynlene-*p*-phenyleneethynylene)s bearing polymerizable diene or norbornene groups were synthesized by the Sonogashira–Hagihara coupling polymerization of the corresponding D-hydroxyphenylglycine-derived diiodo monomers with *p*-diethynylbenzene. These polymers exhibited strong Cotton effects derived from a predominantly one-handed helical conformation in $CHCl_3$ and tetrahydrofuran, but exhibited weak or no Cotton effects in *N*,*N*-dimethylformamide. The metathesis polymerization of the diene and norbornene moieties was performed at the side chains of the polymers under diluted conditions in the presence of a chain-transfer agent, if necessary. The reaction took place intramolecularly, which was confirmed by size exclusion chromatography (SEC) measurements. The polymers exhibited stronger Cotton effects even in polar media after the intramolecular crosslinking, which indicated stabilization of the predominantly one-handed helical structures.

1. Introduction

A helix is a typical regulated secondary structure of biopolymers such as amylose, protein and DNA. Synthetic polymers also form helical structures. A helical structure in artificial polymers was first discovered in isotactic polypropylene synthesized using the Ziegler–Natta catalyst, which dates to the 1950s [1]. Since the discovery of helical poly(triphenylmethyl methacrylate) synthesized by asymmetric anionic polymerization [2], a wide variety of synthetic helical polymers have been reported, including polyacetylenes [3], polyisocyanates [4], polyisocyanides [5], polysilanes [6] and poly(phenyleneethynylene)s [7]. These polymers adopt helical conformations due to non-flexible conjugated backbones and/or steric repulsion between the side chains and garner significant attention because of their possible applications as chiral sensors, asymmetric catalysts and optical resolution materials [8].

We recently synthesized novel poly(*m*-phenyleneethynlene-*p*-phenyleneethynylene)s via the Sonogashira–Hagihara coupling polymerization of D-hydroxyphenylglycine-derived diiodo monomers with *p*-diethynylbenzene [9]. The obtained polymers formed helices with a hydrophobic exterior (due to alkyl groups) and a hydrophilic interior (from phenol groups) in nonpolar solvents. This helical structure was more stable to heating than common poly(phenyleneethynylene)s (i.e., the CD and UV–vis spectroscopic signals exhibited almost no changes between 0 and 50 °C in $CHCl_3$) [10]. The thermal stability was assumed to be brought about by regulated intramolecular hydrogen bonding between the amide groups at the i^{th} and $(i+6)^{th}$ units on the side chains, as well as by amphiphilicity and π-stacking between the phenylene main chains. However, the helical structure was susceptible to polar solvents such as water and methanol, presumably due to collapse of the amphiphilic balance and intramolecular hydrogen bonding strands.

Stability in polar solvents is an important property with respect to the application of D-hydroxyphenylglycine-based helical poly(phenyleneethynylene)s to functional materials. Clipping or crosslinking the side chains of the polymer is effective at stabilizing the conformation.

Hydrocarbon stapling—the ring-closing metathesis of helical peptides bearing olefinic side chains—provides a useful strategy for the experimental and therapeutic modulation of protein–protein interactions in many signaling pathways [11]. Metathesis reactions are also effective for the fixation of self-assembled supramolecules [12]. For example, a helical poly(*m*-phenyleneethynylene) bearing cinnamate groups has been covalently stabilized by [2 + 2] photodimerization reactions at the side chains [13]. Using this methodology, we herein report the synthesis of novel helical poly(phenyleneethynlene)s bearing polymerizable groups at the side chains and their subsequent polymerization to obtain

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polymers that exhibit high helix stability in both nonpolar and polar solvents.

2. Experimental procedure

2.1. Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX-400 or JEOL AL-400 spectrometer. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Mass spectra were measured on a Thermo Fisher Scientific EXACTIVE mass spectrometer. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter. Number- and weight-average molecular weights (M_n and M_w) of polymers were determined by SEC (Shodex columns KF805 × 3) eluted with THF and calibrated using polystyrene standards at 40 °C. CD and UV–vis absorption spectra were recorded on a JASCO J-820 spectropolarimeter.

2.2. Materials

1,6-Heptadienyl-4-amine [14], 2,6-diallyl-4-methylaniline [15] and *N*-(2-aminoethyl)-5-norbornene-*endo,endo*-2,3-dicarboximide [16] were synthesized according to methods reported in the literature. *N*,*N*-Dimethylformamide (DMF), Et_3N, tetrahydrofuran (THF) and $CHCl_3$ were distilled prior to use. All other reagents were commercially obtained and used as received without purification.

2.3. Monomer synthesis

2.3.1. Synthesis of *N*-α-*tert*-butoxycarbonyl-4′-hydroxy-3′,5′-diiodo-D-phenylglycine

This compound was synthesized using a modified literature method [17]. Briefly, ICl (25.0 g, 154 mmol) was added dropwise to a suspension of D-*p*-hydroxyphenylglycine (12.0 g, 71.9 mmol) in AcOH (95 mL) under nitrogen. After the suspension was stirred at room temperature for 72 h, the reaction mixture was poured into ice water (1 L). The precipitated solid was collected by filtration and washed with ice water (500 mL × 2). The filtrate was dried under reduced pressure to afford 4′-hydroxy-3′,5′-diiodo-D-phenylglycine in 65% yield (19.6 g, 46.8 mmol). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.45 [br, 4H, COO*H*, NH_2, O*H*], 7.75 [s, 2H, Ar], 4.24 [s, 1H, C**H*] ppm.

A solution of di-*tert*-butyldicarbonate (DIBOC, TOKUYAMA, 6.64 g, 30.4 mmol) in 1,4-dioxane (50 mL) was added to a solution of 4′-hydroxy-3′,5′-diiodo-D-phenylglycine (10.5 g, 25.1 mmol) and Na_2CO_3 (3.30 g, 31.1 mmol) in H_2O (50 mL) at room temperature. After the resulting solution was stirred overnight, the reaction mixture was concentrated under reduced pressure. AcOEt was added to the residue, and the resulting mixture was extracted with H_2O. The water layer was washed with AcOEt, acidified to pH = 3 by the addition of citric acid and extracted with AcOEt. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford *N*-α-*tert*-butoxycarbonyl-4′-hydroxy-3′,5′-diiodo-D-phenylglycine (11.6 g, 22.3 mmol) in 89% yield. The product was used in the next step without purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 [1H, N*H*], 7.75 [s, 2H, Ar], 5.81 [br, 1H, O*H*], 4.98 [d, *J* = 4.8 Hz, 1H, C**H*], 1.29 [s, 9H, C(CH_3)$_3$] ppm.

2.3.2. Synthesis of monomer **1**

1,6-Heptadienyl-4-amine (2.35 g, 21.1 mmol) and 4-(4,6-dimethoxy-1,3,5-triazine-2-yl)-4-methylmorpholinium chloride (TRIAZIMOCH, TOKUYAMA, 4.55 g, 19.4 mmol) were added to a solution of *N*-α-*tert*-butoxycarbonyl-4′-hydroxy-3′,5′-diiodo-D-phenylglycine (13.2 g, 25.4 mmol) in THF (50 mL) at room temperature. The solution was evaporated after being stirred overnight. To the residue, CH_2Cl_2 was added and washed with 0.5 M HCl, saturated aq. $NaHCO_3$, H_2O and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford a brown solid mass. The residue was purified by silica-gel column chromatography eluted with $CHCl_3$/AcOEt = 19/1 (v/v) and then hexane/AcOEt = 19/1 (v/v), followed by recrystallization to obtain **1** as a yellowish solid. Mp 163–164 °C, $[\alpha]_D$ − 49.4° (*c* = 0.1 g/dL, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 [s, 2H, Ar], 5.82–5.43 [m, 5H, CON*H*, OCON*H*, O*H*, CH_2=C*H*], 5.12–4.82 [m, 5H, C**H*, CH_2=CH], 4.05 [m, 1H, CH_2C*H*], 2.26–2.07 [m, 4H, CH_2], 1.42 [s, 9H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 155.0, 153.6, 138.0, 134.6, 133.8, 133.4, 118.4, 118.3, 82.5, 80.4, 56.7, 48.5, 38.5, 38.2, 28.3 ppm. IR (cm^{-1}, KBr): 3383, 3309, 2977, 2938, 1715, 1644, 1166. HR-ESI-MS (*m*/*z*): $[M + H]^+$ Calcd for $C_{20}H_{27}O_4N_2I_2$: 613.0060, found 613.0044.

2.3.3. Synthesis of monomer **2**

Monomer **2** was synthesized in a manner similar to that used for **1**, except 2,6-diallyl-4-methylaniline was used instead of 1,6-heptadienyl-4-amine. Yield: 40% (yellowish solid). Mp 197–199 °C, $[\alpha]_D$ − 58.9° (*c* = 0.1 g/dL, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 [s, 2H, Ar], 6.90 [s, 2H, Ar], 6.85 [br, 1H, O*H*], 5.82–5.73 [m, 4H, CON*H*, OCON*H*, CH_2=C*H*], 5.10 [br, 1H, C**H*], 5.01 and 4.81 [d, *J* = 10.2 Hz and d, *J* = 17.0 Hz, 4H, CH_2=CH], 3.16–3.03 [m, 4H, CH_2], 2.28 [s, 3H, CH_3], 1.43 [s, 9H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 155.1, 153.8, 137.9, 137.8, 136.8, 136.4, 134.2, 129.8, 128.9, 115.7, 82.8, 80.6, 56.6, 36.3, 28.4, 21.1 ppm. IR (cm^{-1}, KBr): 3313, 2978, 2926, 1660, 1163. HR-ESI-MS (*m*/*z*): $[M + H]^+$ Calcd for $C_{26}H_{31}O_4N_2I_2$: 689.0373, found 689.0355.

2.3.4. Synthesis of monomer **3**

Monomer **3** was synthesized in a manner similar to that used for **1** using *N*-(2-aminoethyl)-5-norbornene-*endo*,*endo*-2,3-dicarboximide instead of 1,6-heptadienyl-4-amine. Yield: 24% (white solid). Mp: 116–118 °C. $[\alpha]_D$ − 66° (*c* = 0.1 g/dL, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 [s, 2H, Ar], 6.36–5.78 [m, 5H, CON*H*, OCON*H*, O*H*, C*H*=C*H*], 4.92 [1H, C**H*], 3.54–3.20 [m, 8H, CONHCH_2CH_2N, C*H*CONCOC*H*, C*H*-CH=CH-C*H*], 1.73 [d, *J* = 9.04 Hz, 1H, bridge position], 1.54 [d, *J* = 8.80 Hz, 1H, bridge position], 1.42 [s, 9H, C(CH_3)$_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 169.5, 154.9, 153.6, 137.9, 134.4, 134.3, 82.7, 80.4, 56.6, 52.3, 45.8, 44.9, 39.8, 37.2, 28.3 ppm. IR (cm^{-1}, KBr): 3311, 2978, 2941, 1693, 1185, 1161. HR-APCI-MS (*m*/*z*): $[M + H]^+$ Calcd for $C_{24}H_{28}O_6N_3I_2$: 708.0067, found708.0058.

2.4. Polymerization

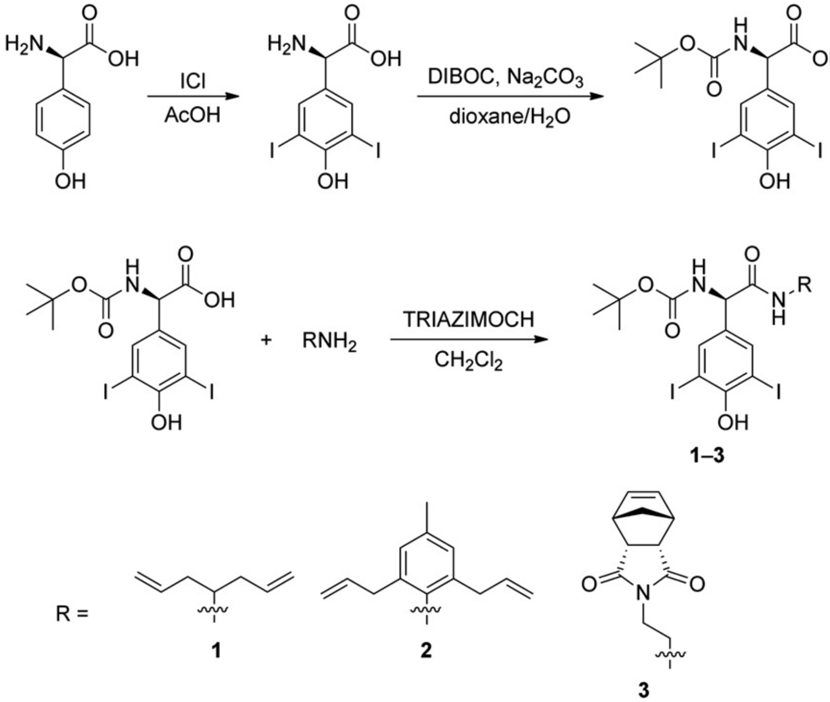
2.4.1. Sonogashira–Hagihara coupling polymerization [9]

Typical procedure: a solution of **1** (1.22 g, 1.99 mmol), *p*-diethynylbenzene (0.251 g, 1.99 mmol), $PdCl_2(PPh_3)_2$ (25.7 mg, 0.0366 mmol), CuI (44.7 mg, 0.235 mmol) and PPh_3 (44.7 mg, 0.170 mmol) in Et_3N (8 mL) and DMF (12 mL) was stirred at 80 °C for 24 h. The reaction mixture was poured into MeOH/acetone [5/1 (v/v), 600 mL]. The precipitate was separated by filtration using a membrane filter (ADVANTEC H100A047A) and then dried under reduced pressure.

2.4.2. Spectroscopic data for polymers

1: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.33 [br, 2H, Ar], 6.08–5.43 [br, 5H, CON*H*, OCON*H*, O*H*, CH_2=C*H*], 5.31–4.58 [br, 5H, C**H*, CH_2=CH], 4.18–3.91 [br, 1H, CH_2C*H*], 2.59–1.98 [br, 4H, CH_2], 1.84–1.09 [br, 9H, C(CH_3)$_3$] ppm.

2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.40 [br, 2H, Ar], 6.98–6.47 [br, 3H, Ar, O*H*], 5.86–5.50 [br, 4H, CON*H*, OCON*H*, CH_2=C*H*],



Scheme 1. Synthesis of monomers **1**–**3**.

5.08–4.53 [br, 5H, $\mathrm{C^{*}}H$, $\mathrm{C}H_2$=CH], 3.22–2.86 [br, 4H, $\mathrm{C}H_2$], 2.37–2.10 [br, 3H, $\mathrm{C}H_3$], 1.84–1.11 [br, 9H, $\mathrm{C(C}H_3)_3$] ppm.

3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.32 [br, 2H, Ar], 6.23–5.69 [br, 5H, CON*H*, OCON*H*, O*H*, C*H*=C*H*], 5.35–5.10 [br, 1H, $\mathrm{C^{*}}H$], 3.88–2.84 [br, 8H, $\mathrm{CONHC}H_2\mathrm{C}H_2\mathrm{N}$, C*H*CONCOC*H*, C*H*-CH=CH-C*H*], 2.01–1.12 [br, 11H, bridge position, $\mathrm{C(C}H_3)_3$] ppm.

2.5. Metathesis polymerization at the side chains

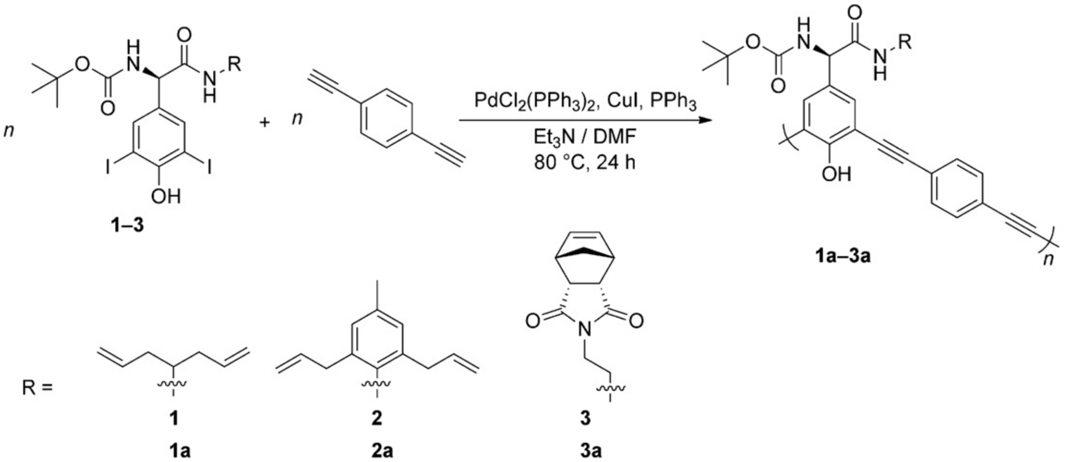
*2.5.1. Acyclic diene metathesis (ADMET) polymerization at the side chains of **1a** and **2a***

A solution of **1a** [26.0 mg, 0.0539 mmol (monomer unit)] and the second-generation Grubbs' catalyst (1.3 mg, 1.5 μmol) in THF (26 mL) was stirred at 45 °C for 18 h. Excess ethyl vinyl ether was added, and the solution was concentrated to a volume of approximately 2 mL. The residual solution was poured into MeOH (100 mL) to precipitate the polymer. The precipitate was filtered using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure. The yield was quantitative. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–6.48 [br, 2H, Ar], 5.92–5.35 [br, 4H, Ar, CON*H*, OCON*H*, C*H*=C*H*], 5.18–4.82 [br, 1H, $\mathrm{C^{*}}H$], 4.09–3.77 [br, 1H, $\mathrm{CH_2C}H$], 2.46–1.85 [br, 4H, $\mathrm{C}H_2$], 1.83–0.87 [br, 9H, $\mathrm{C(C}H_3)_3$] ppm.

The ADMET reaction for the preparation of **2b** was performed in a manner analogous to that used for **1a** in $CHCl_3$ at 50 °C for 24 h. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.88–7.39 [br, 2H, Ar], 6.97–6.61 [br, 3H, Ar, O*H*], 5.90–5.47 [br, 4H, Ar, CON*H*, OCON*H*, C*H*=C*H*], 5.04–4.54 [br, 1H, $\mathrm{C^{*}}H$], 3.24–2.95 [br, 4H, $\mathrm{C}H_2$], 2.46–2.05 [br, 3H, $\mathrm{C}H_3$], 2.03–0.92 [br, 9H, $\mathrm{C(C}H_3)_3$] ppm.

*2.5.2. Ring-opening metathesis polymerization (ROMP) at the side chains of **3a***

A solution of **3a** [116 mg, 0.200 mmol (monomer unit)], second-generation Grubbs' catalyst (11.1 mg, 13.1 μmol) and *cis*-1,4-dichloro-2-butene (20 μL, 0.19 mmol) as a chain-transfer agent in



Scheme 2. Sonogashira–Hagihara coupling polymerization of **1**–**3** with *p*-diethynylbenzene.

Table 1
Polymerization of **1**–**3** with *p*-diethynylbenzene.[a]

Monomer	Yield[b] (%)	M_n[c]	PDI[c]
1	72	6300	2.4
2	64	6300	2.4
3	96	6700	2.0

[a] Conditions: $[\mathbf{1}\text{–}\mathbf{3}]_0$ = [*p*-diethynylbenzene]$_0$ = 0.1 M, $[PdCl_2(PPh_3)_2]$ = 0.002 M, [CuI] = 0.012 M, $[PPh_3]$ = 0.008 M in Et_3N/DMF (2/3,v/v), 80 °C, 24 h.
[b] MeOH/acetone = 5/1 (v/v)—insoluble fraction.
[c] Determined by SEC eluted with THF and calibrated with polystyrene standards.

THF (100 mL) was stirred at 50 °C for 24 h [18]. The solution was then concentrated to a volume of approximately 2 mL. The residue was poured into MeOH (100 mL) to precipitate the polymer, which was collected using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53–6.87 [br, 2H, Ar], 6.36–5.59 [br, 3H, CON*H*, OCON*H*, O*H*], 5.51–5.00 [br, 3H, C*H*=C*H*, C**H*], 4.41–2.90 [br, 8H, CONHC*H*$_2$C*H*$_2$N, C*H*CONCOC*H*, C*H*-CH=CH], 2.58–0.86 [br, 11H, CH-C*H*$_2$-CH, C(C*H*$_3$)$_3$] ppm.

3. Results and discussion

3.1. Monomer synthesis

Monomers **1**–**3** were successfully synthesized by the condensation of *N*-α-*tert*-butoxycarbonyl-4′-hydroxy-3′,5′-diiodo-D-phenylglycine with the corresponding amines bearing diene and norbornene moieties (Scheme 1). *N*-α-*tert*-bButoxycarbonyl-4′-hydroxy-3′,5′-diiodo-D-phenylglycine was synthesized by diiodation of hydroxy-D-phenylglycine using ICl followed by *N*-*tert*-butoxycarbonylation using DIBOC. All the monomers were obtained as yellowish-white powders and were characterized by ^{1}H, ^{13}C NMR, IR and high-resolution mass spectrometry.

3.2. Polymerization

The Sonogashira–Hagihara coupling polymerization of **1**–**3** with *p*-diethynylbenzene afforded the corresponding poly(*m*-phenyleneethynlene-*p*-phenyleneethynlene)s **1a**–**3a** that bear polymerizable groups at the side chains with M_n values that range from 6300 to 6700 (PDI = 2.0–2.4) in 64–96% yields (Scheme 2, Table 1). The polymers were soluble in $CHCl_3$, THF, DMF and DMSO, but insoluble in hexane and MeOH.

3.3. Chiroptical properties

The CD and UV–vis spectra of **1a**–**3a** were measured in $CHCl_3$, THF and DMF at room temperature to obtain information on the secondary structures. All of the polymers exhibited strong split Cotton effects in $CHCl_3$ and THF (Fig. 1). The CD and UV–vis signals allowed the assignment of a chirally ordered conjugated polymer main chain because the λ_{max} values of the polymers appeared at longer wavelengths than those of the monomers (**1**–**3**: λ_{max} = 224 nm) and *p*-diethynylbenzene (λ_{max} = 276 nm). The inflection point from the first positive to second negative CD sign agreed with the λ_{max} from the UV–vis absorption, which indicated the CD split was caused by exciton coupling of the chromophores [19]. The polymer solutions exhibited the same CD and UV–vis spectroscopic patterns after they were filtered using a PTFE membrane with a pore size of 0.45 μm [20], and patterns exhibited no concentration dependence in the range from 0.02 to 0.05 mM. Therefore, the CD signals probably originated predominantly from right-handed helical conformations instead of from chirally aggregated structures [21].

In DMF, **1a** and **2a** exhibited Cotton effects weaker than those in $CHCl_3$ and THF, and **3a** did not exhibit Cotton effects. The λ_{max}s of **1a**–**3a** red-shifted in DMF compared to those in $CHCl_3$ and THF, but the degree of red-shift is much smaller than the cases regarding transformation of helical poly(phenyleneethynylene)s into random ones [22]. This fact indicates that the small CD intensities of the present polymers in DMF compared to those in $CHCl_3$ and THF are mainly caused by the decrease of helix sense predominance, and partly caused by transformation of helix into random coil. The low one-handed helicity in DMF is explainable by the higher polarity of DMF relative to the other two solvents; the higher polarity of DMF led to a collapse of regulated >N–H•••O=C< hydrogen bonding strands between the side chains, which play an important role in helix formation [9,23]. This hypothesis was also supported by the CD and UV–vis spectroscopic measurements of **3a** in a mixed solvent of THF/H_2O (see the Supplementary content, Fig. S1). Specifically, the Kuhn's dissymmetry factor (*g* value = $\Delta\varepsilon/\varepsilon$, in which $\Delta\varepsilon = [\theta]/3298$) of **3a** decreased with increasing H_2O content and approached 0 when the H_2O content reached 10% as shown in

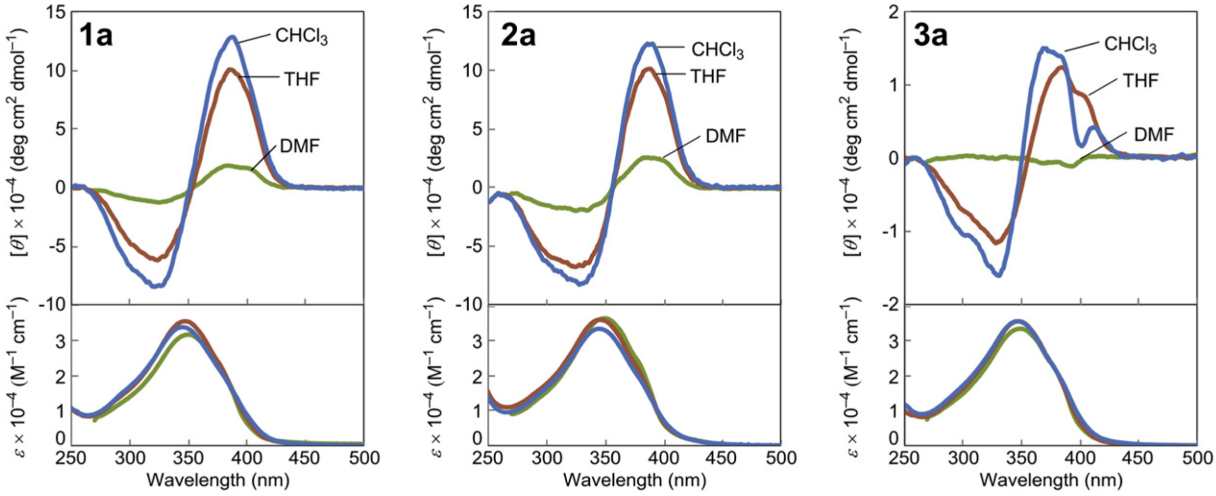


Fig. 1. CD and UV–vis spectra of **1a**–**3a** measured in $CHCl_3$, THF and DMF at room temperature (c = 0.03 mM).

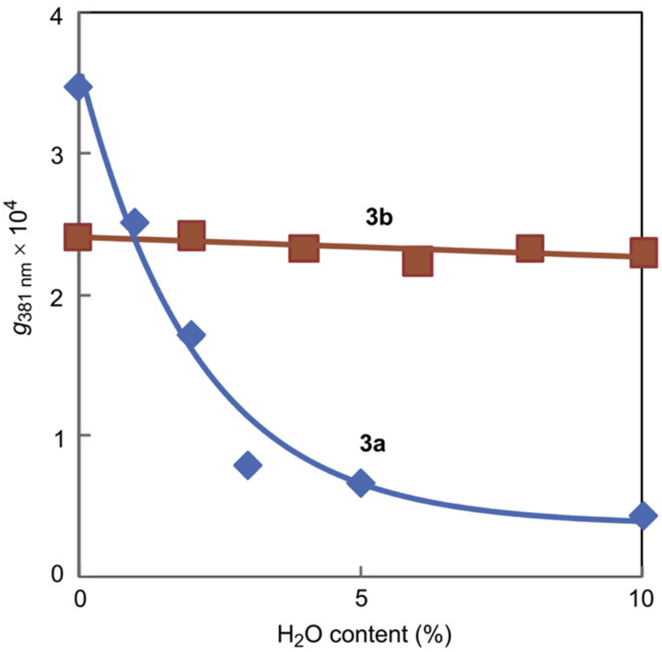


Fig. 2. Relationship between *g* values at 381 nm and H_2O content [H_2O/(H_2O + THF), volume ratio] of a solution of **3a** and **3b** in THF/H_2O (c = 0.03 mM) at room temperature.

Fig. 2. Therefore, the helicity of **3a** was highly susceptible to the polarity of solvents.

3.4. Polymerization at the side chains

Polymers **1a** and **2a** were subjected to ADMET polymerization using the second-generation Grubbs' catalyst in THF and $CHCl_3$, respectively. The polymerizations were performed at high dilution [2 mM (monomer unit)] to suppress intermolecular reactions. The progress of ADMET (Scheme 3, top) was followed by ^{1}H NMR spectroscopic measurements (see the Supplementary content, Fig. S2). The ADMET conversion of **2a** was determined to be 10% (see the Supplementary content, Note S1). No significant changes in M_n or PDI values (Table 2) were observed before and after ADMET, which indicates the absence of intermolecular crosslinking and side reactions, such as metathesis reactions, that involve the triple bonds of the main chain. The conjugation through the triple bonds and steric hindrance appear to effectively suppress such side reactions.

Polymer **3a** was subjected to ROMP using the second-generation Grubbs' catalyst in THF (see the Supplementary content, Note S2). In this case, *cis*-1,4-dichloro-2-butene was added as a chain-transfer agent because the degree of polymerization at the side chains was expected to be no more than 2 based on the M_n of **3a** (see the Supplementary content, Note S3). The conversion of the norbornene moieties was 60%, which was determined by ^{1}H NMR spectroscopy (see the Supplementary content, Fig. S3). Based on the SEC data, the reaction did not take place intermolecularly, but intramolecularly in a fashion similar to the previously discussed ADMET of **1a** and **2a**.

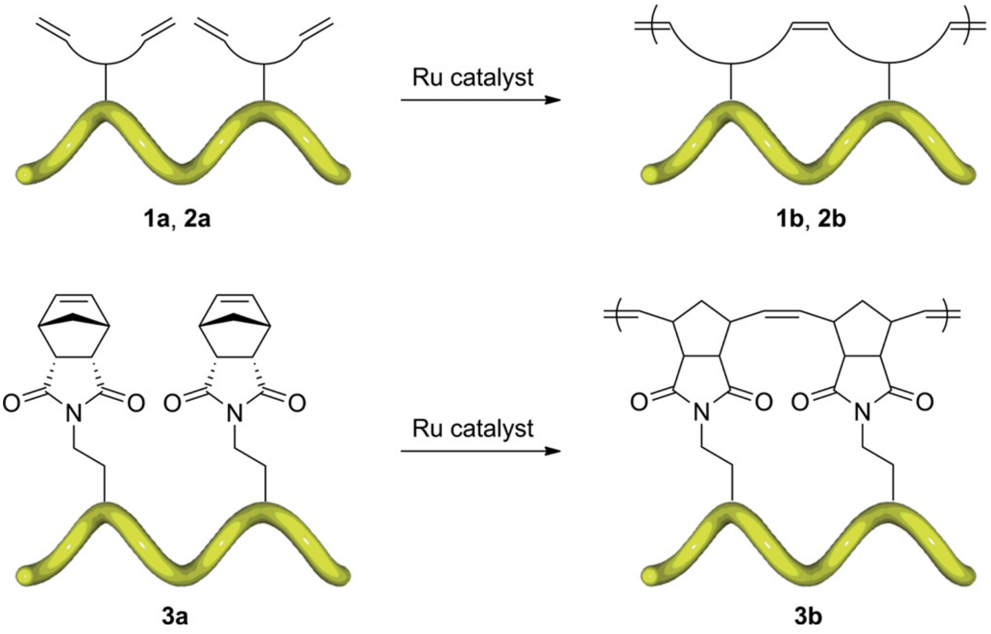
3.5. Chiroptical properties of the polymers after metathesis

Fig. 3 depicts the CD and UV–vis spectra of polymers **1b**–**3b** obtained from metathesis at the side chains of **1a**–**3a**. No

Table 2
Metathesis reactions of **1a**–**3a**.[a]

Polymer	Before metathesis		[Ru][b] (mM)	Solvent	Temp (°C)	Time (h)	After metathesis		
	M_n	PDI					Yield[c] (%)	M_n[d]	PDI[d]
1a	6300	2.4	0.06	THF	45	18	Quant	5900	2.2
2a	6300	2.4	0.08	$CHCl_3$	50	24	80	6900	2.0
3a[e]	6700	2.0	0.13	THF	50	24	93	6600	1.8

[a] $[M]_0$ = 2 mM (monomer unit).
[b] Grubbs' second-generation catalyst.
[c] MeOH-insoluble fraction.
[d] Determined by SEC eluted with THF and calibrated with polystyrene standards.
[e] *cis*-1,4-Dichloro-2-butene (2 mM) was added.



Scheme 3. ADMET and ROMP at the side chains of **1a**–**3a**.

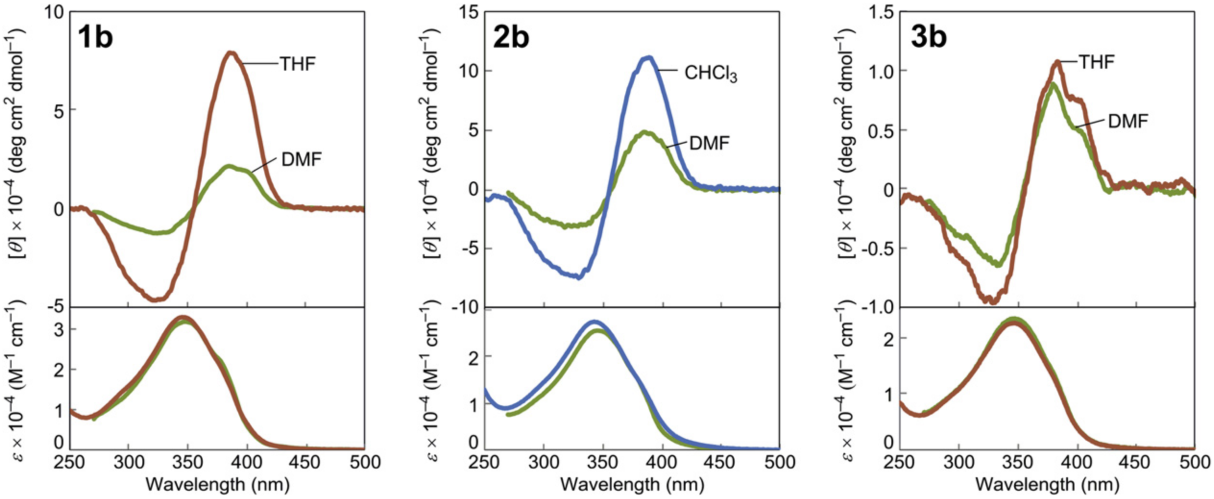


Fig. 3. CD and UV–vis spectra of **1b**–**3b** measured in CHCl$_3$, THF and DMF at room temperature (c = 0.03 mM).

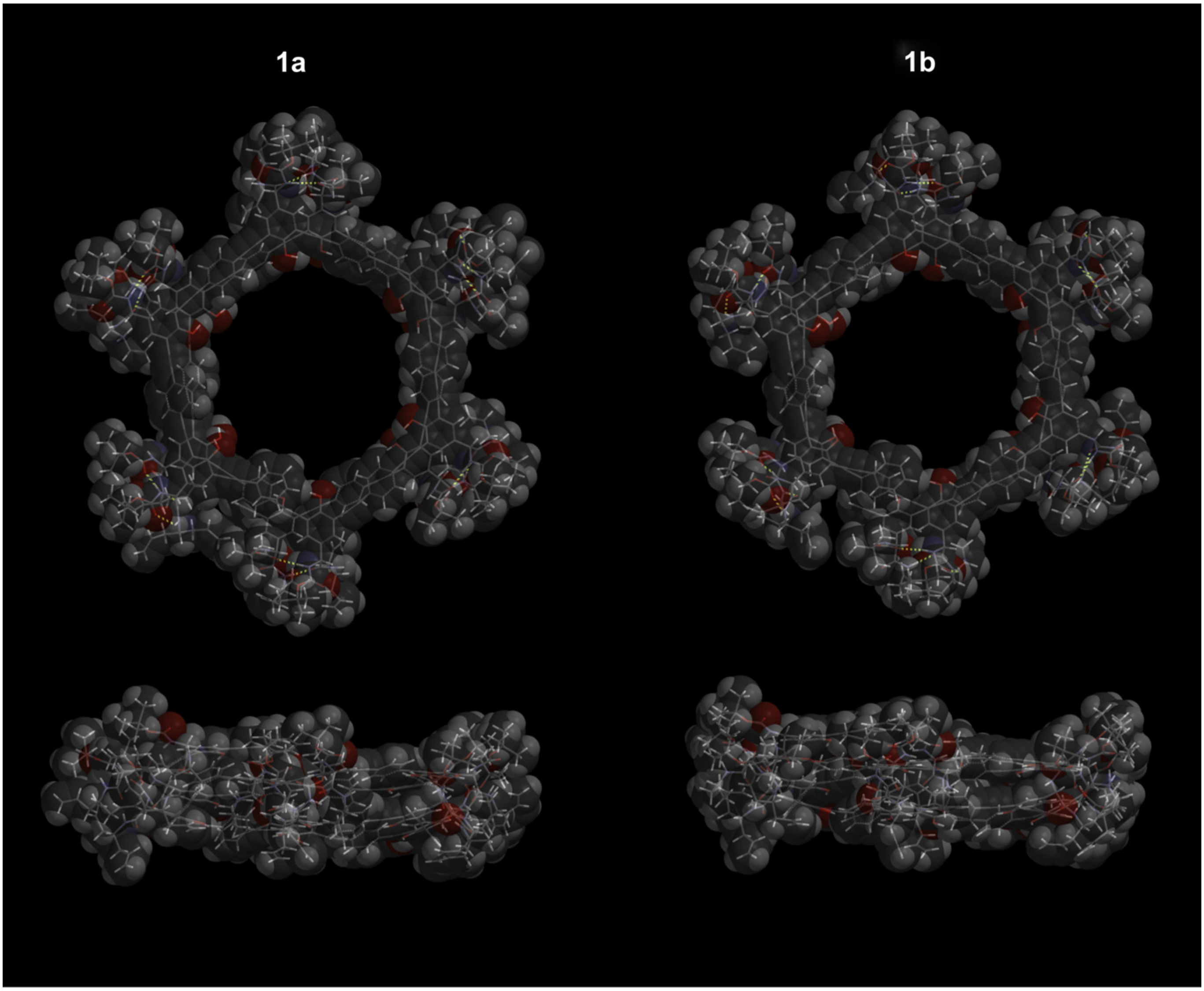


Fig. 4. Top and side views of possible conformers **1a** and **1b** (12-mers). Geometries were fully optimized using the MMFF94 method.

significant difference was observed between the intensities of the Cotton effects of **1a** and **1b** measured in THF and those of **2a** and **2b** measured in $CHCl_3$, whereas the intensities of **1b** and **2b** became larger than those of **1a** and **2a** in DMF. These results suggested that the helical structures were partly fixed by ADMET polymerization and that the stability toward DMF was partly enhanced. These results were also supported by the comparison of CD intensities of **1a** and **1b** in DMF/THF (19% and 27%) and those of **2a** and **2b** in DMF/$CHCl_3$ (21% and 44%).

The difference between **1a** → **1b** (+8%) and **2a** → **2b** (+23%) was presumably caused by the difference in degrees of ring-closing metathesis (RCM). As noted (see the Supplementary content, Note S1), **1a** was more likely to induce RCM than was **2a**, which resulted in better helix stability for **1b** than for **2b**.

The trend of helix stabilization was apparent in the conversion of **3a** to **3b**. In DMF, **3a** exhibited no CD signal, whereas **3b** exhibited signals comparable in intensity to that in THF. Thus, we concluded that the helix stability of **3b** was greatly enhanced due to intramolecular crosslinking by ROMP. This conclusion was also confirmed by the CD and UV–vis spectra measured in mixed THF/H_2O solvent. The Kuhn's dissymmetry factor (g value) of **3a** remarkably decreased when the H_2O content was increased from 0 to 10% (Fig. 2). In contrast, the g value of **3b** only slightly decreased when the H_2O content was increased. These results clearly indicated that helix stability was enhanced by ROMP at the side chains.

3.6. Conformation analysis

The conformations of **1a**–**3b** were analyzed using the MMFF94 method [24]. Based on the first positive and second negative exciton-coupled CD signals (Figs. 1 and 3), the polymers adopted a predominantly right-handed helical conformation. Fig. 4 depicts the top and side views of 12-mers of **1a** and **1b** (see the Supplementary content, Figs S4 and S5 regarding **2a**–**3b**). In each case, the conformer formed a helically folded structure, and each turn consisted of six monomer units. The interatomic distance between the i^{th} amide carbonyl oxygen and the $(i + 6)^{\text{th}}$ amide hydrogen ($>C{=}O{\bullet\bullet\bullet}H{-}N<$) was approximately 2 Å (i.e., the amide groups of the polymers formed $i + 6 \rightarrow i$ intramolecular hydrogen bonds). The carbamate groups also formed hydrogen bonds in a similar fashion. The interatomic distances between the diagonal oxygen atoms and the pitch of the helix were 20–22 Å and 4 Å, respectively. The helical structures appeared to be stabilized by hydrogen bonding and π-stacking between the aromatic rings. Intramolecular ADMET and ROMP likely occurred between the monomer units at the i^{th} and $(i + 6)^{\text{th}}$ positions as well. The conformational changes were negligible before and after the metathesis reactions, which indicated smooth reactions.

4. Conclusions

In this paper, we have demonstrated the synthesis of novel helical poly(phenyleneethynylene)s **1a**–**3a** that bear polymerizable diene or norbornene groups at the side chains. All of the polymers exhibited first positive and second negative Cotton effects based on exciton coupling of the conjugated main chain in $CHCl_3$ and THF. We concluded that the polymers adopted a predominantly right-handed helical conformation in these solvents. However, the polymers exhibited only weak or no Cotton effects in DMF. We assumed that intramolecular hydrogen bonding at both the amide and carbamate groups between the side chains was effective at stabilizing the helical conformation. Polymers **1a** and **2a** bearing diene moieties were subjected to ADMET, and polymer **3a** bearing norbornene moieties was subjected to ROMP at the side chains using the second-generation Grubbs' catalyst. After ADMET and ROMP at the side chains, the M_n values of the polymers were unchanged, which indicated that the metathesis reactions occurred intramolecularly, not intermolecularly. The synthesized polymers exhibited more intense Cotton effects in DMF than did the polymers prior to metathesis. Interestingly, **3b** exhibited CD signals in DMF comparable in intensity to those taken in THF. Moreover, the g value of **3b** was almost constant in a THF/H_2O mixed solvent at any composition. These results indicated that the predominantly one-handed helical conformation of **3b** was successfully fixed by intramolecular ROMP. We are currently investigating the chiral recognition properties of polymers with fixed conformations.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2012.04.028.

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