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ORIGINAL PAPER

Synthesis of chiral side-chain liquid crystalline polyacetylenes bearing succinic acid spacer

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Abstract A chiral acetylene monomer having a cholesteryl group (PSCh) and novel three types of chiral acetylene monomers having a *o*-substituted tyrosine methyl ester (PSMY-Rs: $-COC_6H_5$=PSMY-Bz; $-COC_6H_4CN$=PSMY-BzCN; $-COC_{12}H_9$=PSMY-PhBz) as a pendant group were synthesized from 4-oxo-4-(prop-2-ynyloxy)butanoic acid (PS), and polymerized with the rhodium-catalyzed system. Structures and properties of the monomers and the resulting polymers were characterized and evaluated by NMR, IR, GPC, and DSC. In addition, these optical properties were investigated by polarimetric detector and circular dichroism (CD) analyses.

Keywords Polyacetylene · Rhodium catalyst · Liquid crystalline polymer · Cholesterol · Tyrosine

Introduction

Chiral liquid crystalline materials have generally high spontaneous polarization and fast response. Thus, these materials can show a variety of characteristic behavior on application of electric and magnetic fields such as display devices and storage [1].

A cholesteryl group is a promising functional group leading polymers to exhibit LC properties. Liquid crystalline polymers (LCPs) comprising helically ordered cholesterol side-chains have the ability of reflecting certain frequency range of

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incoming polarized light. This selective light reflection and the tuning of the helical pitch in these chiral nematic LCPs have been applied for the development of electro-optical devices, nonlinear optical materials, tunable mirror less-lasing and optical data, or color recording devices. In addition, biodegradable polyesters with cholesterol end-groups can be used as membranes for cell attachment, proliferation, polymeric scaffolds, and materials with improved blood compatibility [2, 3].

Besides the cholesteryl group, L-amino acid is an easily obtained nature material, so introducing amino acid derivatives into molecular structure is a convenient way to obtain chiral liquid crystalline materials. Tang et al. [1] reported a route to introduce L-tyrosine derivatives into polysiloxane backbones. However, these have been few reports on chiral liquid crystalline polymers using amino acid derivatives.

Helical polymers have precisely ordered architectures, wide potential applications including molecular recognition, and LC formation through well-ordered molecular alignment. The helix can be found among the most sophisticated and fundamental structures of the polymer chain because its characteristic features can be expected for synthetic helical polymers [4]. Among the synthetic helical polymers, polyacetylenes have been extensively studied. Moore et al. [5] reported that polyacetylenes with a chiral substituent have predominantly a single sense of helix due to the nonplanar conformation of the polyene structure. Yashima et al. [6] reported several unique chirality-responsive helical polymers, such as *cis-transoidal* poly(phenylacetylenes) bearing functional pendant groups as an excess of a single-handed helix through noncovalent bonding interaction. Akagi et al. [7] also reported *trans* polyacetylene obtained in chiral LC reaction field was shown by scanning electron microscopy to consist of single-handed helical structure of fibrils. In addition, a bonding group in the side chain of liquid crystal polymer also influences the liquid crystalline properties due to the geometric and electronic asymmetry. Remarkably, the thermal behavior of smectic-phase liquid crystals is strongly influenced by the orientation of bonding groups and the relatively short-range interactions such as dipole–dipole or dipole-induced-dipole interactions, in addition to van der Waals attraction. In bonding groups, ester group can influence geometric structure or electrostatic properties due to their geometric and electronic asymmetry.

Recently, we reported syntheses and polymerizations of novel acetylene monomers (4-oxo-4-(prop-2-ynyloxy)butanoic acid derivatives; PSRs) having a phenyl or biphenyl moiety as an achiral mesogenic group and succinic acid as a spacer consisting of ester bonding [8]. As a result, PSRs bearing 4-cyanobiphenyl moiety exhibited the smectic phase, and the corresponding polymer exhibited the namatic phase. In this study, to investigate the effect of ester bonding on liquid crystalline properties of liquid crystalline polyacetylenes, we will focus on the synthesis and characterization of novel chiral side-chain liquid crystalline (SCLC) polyacetylenes with succinic acid as a spacer, and cholesterol or tyrosine derivatives were chosen as a chiral mesogenic group. The polymerizabilities of the 4-oxo-4-(prop-2-ynyloxy)butanoic acid derivatives (PSRs) and liquid crystallinity of the polymers were investigated.

Experimental

Materials

Unless otherwise stated, reagents were purchased from commercial suppliers and used without purification. Tetrahydrofuran (THF) and toluene used for polymerization was distilled using the standard procedure before use. (nbd)$Rh^{+}[\eta^{6}$–(C_6H_5)–$B^{-}(C_6H_5)_3]$ (Rh**2**) was prepared from $[Rh(nbd)Cl]_2$ (Rh**1**) according to the literature [9].

Monomer synthesis

Synthesis of 4-oxo-4-(prop-2-ynyloxy)butanoic acid (PS) [10]

2-Propyn-1-ol (12.0 g, 0.214 mol) and succinic acid anhydride (21.4 g, 0.214 mol) of acetic acid (150 mL) solution were refluxed at 120 °C for 10 h, and the acetic acid was evaporated out. The reaction mixture was extracted by each of chloroform and ethyl acetate, the resulting solution was evaporated. The title compound was obtained as pale yellow solid in a yield of 70% with a m.p. of 54 °C.

^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 4.71 (d, 2H, CH_2–COO), 2.71–2.68 (m, 4H, –CH_2–CH_2–), 2.50 (t, 1H, ≡C*H*).

Synthesis of 4-oxo-4-(prop-2-ynyloxy)butanoic acid cholesteryl ester (PSCh) [11].

PS (3.00 g, 19.2 mmol) of $SOCl_2$ solution (15 mL) was stirred at room temperature for 5 h, and unreacted $SOCl_2$ was evaporated out. The residual products were dissolved in 50 mL of benzene. This solution was added dropwise to a benzene solution (120 mL) of cholesterol (8.62 g, 22.3 mmol) and Et_3N (3.13 mL, 22.3 mmol). The reaction mixture was stirred at 0 °C for 1 h and heated at 80 °C for 10 h. After reaction, benzene was evaporated, and the residual products were dissolved in ethyl acetate. The solution was washed with 0.1 N HCl aq. (100 mL), distilled water (100 mL × 3) and saturated $NaHCO_3$ aq. (100 mL), and the combined ethyl acetate was dried over Na_2SO_4. The solution was concentrated and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 2/1) to obtain to PSCh as a white solid in a yield of 24% with a m.p. of 105 °C.

$[\alpha]_{435} = -51.8°$ in THF.

^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 5.38–5.36 (m, 1H, C = C*H*), 4.71 (s, 2H, CH_2), 4.70–4.57 (m, 1H, OC*H*), 2.71–2.59 (q, 4H, –CH_2–CH_2–), 0.47 (s, 1H, ≡C*H*), 2.33–0.68 (m, 43H, cholesteryl protons).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.60, 171.43 (2C, –*C*OO–), 139.56 (1C, >*C*=CH–), 122.72 (1C, –*C*H=C<), 77.44 (1C, –*C*≡CH), 74.95 (1C, >*C*H–), 74.49 (1C, –C≡*C*H), 56.69, 56.14, 52.17, 50.01, 42.32, 39.73, 39.52, 38.03, 36.95, 36.58, 36.18, 35.79, 31.90, 31.86, 29.34, 29.00, 28.23, 28.01, 27.72, 24.28, 23.83, 22.82, 22.56, 21.03, 19.31, 18.72, 11.86 (27C).

Synthesis of *N*-(prop-2-ynyloxy)butanoic-L-tyrosine methyl ester (PSMY)

$SOCl_2$ (12.0 mL, 0.170 mol) was added dropwise to MeOH solution (54 mL) of L-Tyrosine (6.00 g, 33.0 mmol) at −5 °C. The reaction mixture was stirred at room

temperature for 4 h. After reaction, unreacted agent was evaporated. To the ethyl acetate suspension of residual product, Et_3N (5.51 mL, 0.400 mol) was added dropwise and stirred at room temperature overnight. To the solution, 100 mL of water was added and extracted with ethyl acetate (100 mL × 3), and the combined ethyl acetate was dried over $MgSO_4$ anhydride to obtain L-tyrosine methyl ester.

PS (1.62 g, 10.4 mmol) of $SOCl_2$ solution (3.42 mL) was stirred at room temperature for 5 h, and unreacted $SOCl_2$ was evaporated out. The residual products were dissolved in 5 mL of THF. This solution was added dropwise to a benzene solution (120 mL) of L-tyrosine methyl ester (1.84 g, 9.43 mmol) and Et_3N (1.57 mL, 11.3 mmol). The reaction mixture was stirred at 0 °C for 1 h and heated at room temperature overnight. After reaction, THF was evaporated. To the residual product of ethyl acetate solution, 0.1 N HCl aq. (100 mL) was added and extracted with ethyl acetate (100 mL × 3) to obtain PSMY as a white solid in a yield of 85%.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.94–6.73 (m, 4H, Ar–*H*), 6.37–6.24 (br, 1H, –N*H*–), 4.93–4.80 (m, 1H, >C**H*–), 4.67 (s, 2H, ≡C–CH_2–), 3.72 (s, 3H, OCH_3), 3.12–2.92 (m, 2H, C*H–CH_2–), 2.81–2.51 (m, 4H, –CH_2–CH_2–), 2.47 (t, 1H, ≡C*H*).

Synthesis of *N*-(prop-2-ynyloxy)butanoic-*o*-benzoyl-L-tyrosine methyl ester (PSMY-Bz)

$SOCl_2$ (4.51 mL) was added dropwise to benzoic acid (1.90 g, 15.6 mmol), and stirred at 60 °C for 5 h. After reaction, unreacted agent was evaporated. To the THF solution (10 mL) of PSMY (3.47 g, 10.4 mmol) and Et_3N (2.56 mL, 18.7 mol), the residual product of THF (5 mL) solution was added dropwise and stirred at room temperature overnight. After reaction, THF was evaporated. To the residual product of ethyl acetate solution, 0.1 N HCl aq. (100 mL) was added and extracted with ethyl acetate (100 mL × 3), and the combined ethyl acetate was dried over $MgSO_4$ anhydride. The solution was concentrated and purified by column chromatography (silica gel, *n*-hexane/EtOAc = 1/1) to obtain to PSMY-Bz as a white solid in a yield of 44% with a m.p. of 111.3 °C.

$[\alpha]_{435} = +88.1°$ in THF.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.25–7.20 (m, 9H, Ar–*H*), 6.17–6.05 (br, 1H, –N*H*–), 4.94–4.86 (m, 1H, >C**H*–), 4.70 (d, 2H, ≡C–CH_2–), 3.75 (s, 3H, –COOCH_3), 3.24–2.61 (m, 4H, –CH_2–CH_2–), 2.58–2.50 (m, 2H, C*H–CH_2–), 2.47 (t, 1H, ≡C*H*).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.79, 171.70, 170.67, 164.93 (4C, –*C*OO–), 149.85, 133.48, 130.19, 129.96, 129.29, 128.43, 121.62 (12C, Ar), 77.46 (1C, –*C*≡CH), 74.93 (1C, –C≡*C*H), 53.09 (1C, >*C**H–), 52.22 (1C, ≡C–*C*H_2–), 52.01 (1C, –O–*C*H_3), 37.06 (1C, >C*H–*C*H_2–), 30.29, 28.88 (2C, –*C*H_2–COO).

Synthesis of *N*-(prop-2-ynyloxy)butanoic-*o*-(4-cyano-benzoyl)-L-tyrosine methyl ester (PSMY-CNBz)

PSMY-CNBz was synthesized in a manner similar to the synthesis of PSMY-Bz, described above, and obtained as a white solid in 65% yield with a m.p. of 134.6 °C.

$[\alpha]_{435} = +88.1°$ in THF.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.35–7.16 (m, 8H, Ar–*H*), 6.17–6.11 (br, 1H, –N*H*–), 4.95–4.89 (m, 1H, >C***H*–), 4.72 (d, 2H, ≡C–CH_2–), 3.77 (3H, s, –COOCH_3), 3.26–2.66 (m, 4H, –CH_2–CH_2–), 2.58–2.53 (m, 2H, C***H–CH_2–), 2.49 (t, 1H, ≡C*H*).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.88, 171.70, 170.67, 163.43 (4C, –*C*OO–), 149.53, 134.06, 133.25, 132.35, 130.54, 130.45, 121.44, 117.75 (12C, Ar), 116.96 (1C, –*C*≡N), 77.49 (1C, –*C*≡CH), 74.96 (1C, –C≡*C*H), 53.13 (1C, >*C**H–), 52.36 (1C, ≡C–*C*H_2–), 52.14 (1C, –O–*C*H_3), 37.20 (1C, >C*H–*C*H_2–), 30.45, 28.96 (2C, –*C*H_2–COO).

Synthesis of *N*-(prop-2-ynyloxy)butanoic-*o*-(4-phenyl-benzoyl)-L-tyrosine methyl ester (PSMY-PhBz)

PSMY-PhBz was synthesized in a manner similar to the synthesis of PSMY-Bz, described above, and obtained as a white solid in 68% yield with a m.p. of 136.5 °C.

$[\alpha]_{435} = +86.9°$ in THF.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.29–7.17 (m, 13H, Ar–*H*), 6.15–6.10 (br, 1H, –N*H*–), 4.94–4.88 (m, 1H, >C***H*–), 4.71 (d, 2H, ≡C–CH_2–), 3.75 (s, 3H, –COOCH_3), 3.23–2.66 (m, 4H, –CH_2–CH_2–), 2.57–2.52 (m, 2H, C***H–CH_2–), 2.48 (t, 1H, ≡C*H*).

^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 171.90, 171.77, 170.68, 164.98 (4C, –*C*OO–), 150.07, 146.36, 139.79, 133.47, 130.66, 130.35, 128.97, 128.38, 128.32, 128.13, 127.29, 127.22, 121.82 (18C, Ar), 77.54 (1C, –*C*≡CH), 74.98 (1C, –C≡*C*H), 53.18 (1C, >*C**H–), 52.39 (1C, ≡C–*C*H_2–), 52.20 (1C, –O–*C*H_3), 37.23 (1C, >C*H–*C*H_2–), 30.54, 29.03 (2C, –*C*H_2–COO).

Polymerizations

*Polymerization with [Rh(nbd)Cl]$_2$ (Rh**1**)*

PSR (0.30 g) was added to a Schlenk flask, and placed under an N_2 atmosphere. And then Et_3N (1.0 equiv.) and polymerization solvent (THF or toluene) was added. [Rh(nbd)Cl]$_2$ (Rh**1**, 0.01 equiv.) was added to a pear-shaped flask, placed under an N_2 atmosphere, and dissolve in polymerization solvent. The Rh**1** solution was added to monomer solution, and the mixture was vigorously stirred.

Upon complete polymerization, methanol was added to quench the polymerization. The solutions were concentrated and purified three times by reprecipitation from THF in methanol. The polymers were dried in a vacuum oven at room temperature for 3 days.

*Polymerization with (nbd)Rh$^+$[η^6–(C_6H_5)–B$^-$(C_6H_5)$_3$] (Rh**2**)*

PSR (0.30 g) was added to a Schlenk flask, placed under an N_2 atmosphere, and dissolve in polymerization solvent. (nbd)Rh$^+$[η^6–(C_6H_5)–B$^-$(C_6H_5)$_3$] (Rh**2**, 0.01 equiv.) was added to a pear-shaped flask, placed under an N_2 atmosphere, and

dissolve in polymerization solvent. The Rh**2** solution was added to monomer solution, and the mixture was vigorously stirred.

Upon complete polymerization, methanol was added to quench the polymerization. The solutions were concentrated and purified three times by reprecipitation from THF in methanol. The polymers were dried in a vacuum oven at room temperature for 3 days.

Measurements

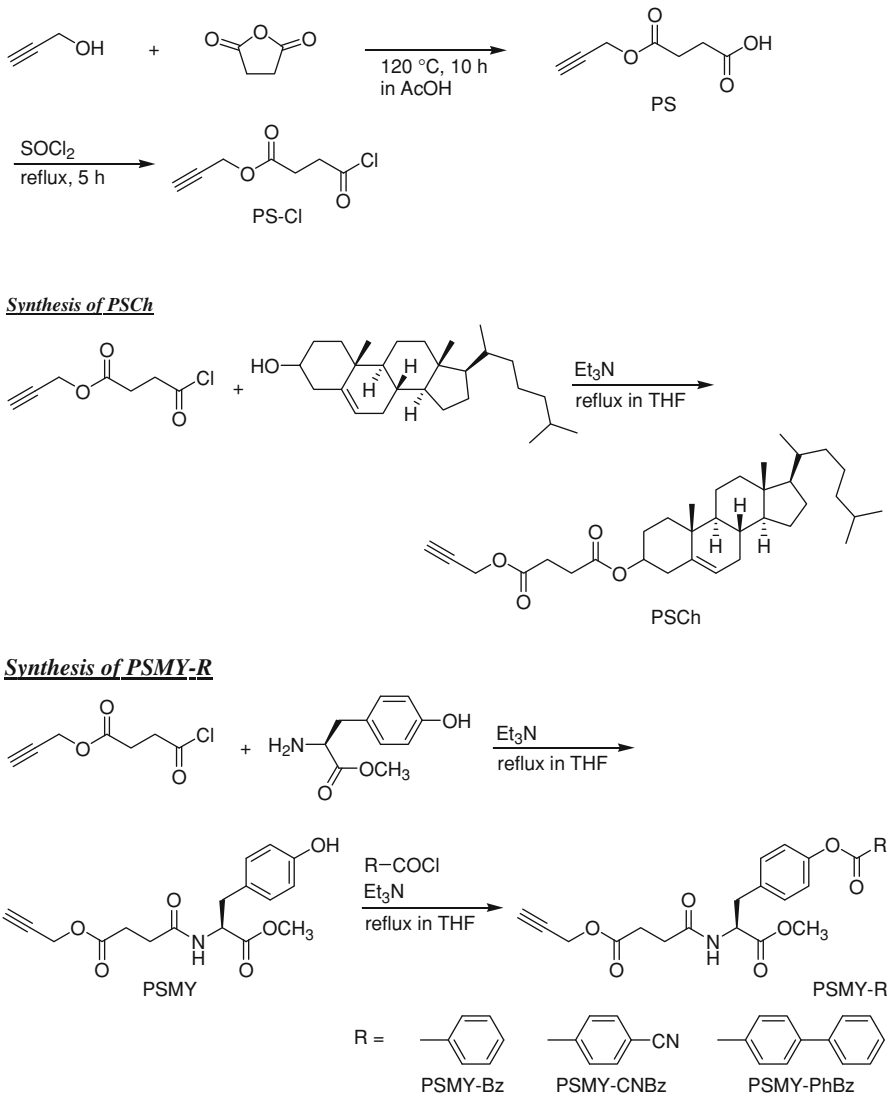
^{1}H and ^{13}C NMR spectra were recorded using tetramethylsilane as an internal standard in $CDCl_3$ on a JEOL GSX-500 spectrometer. Specific rotations ($[\alpha]_{435}$) were measured by a JASCO P-1030 digital polarimeter. The number- and weight-average molecular weights (M_n and M_w) of polymers were determined by gel permeation chromatography (GPC) on a CHROMATOPAC C-R7A plus (LC-10AS, CTO-2A, SPD-10A, JASCO OR-990) equipped with polystyrene gel columns (HSG-40G, HSG-20H, HSG-15H, and HSG-10H), using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL min^{-1}, calibrated by polystyrene standards at 50 °C. The phase transition temperatures were determined with a DSC 3100 equipped with a liquid nitrogen cooling system at a constant heating/cooling rate of 10 °C/min. Optical texture observation was performed using a OLYMPUS BHSP polarizing optical microscope equipped with a METTLER FP82 HT hot stage.

Results and discussion

Syntheses and polymerizations of acetylene-based monomers

Acetylene monomers bearing a cholesteryl group or tyrosine derivatives as a pendant group (PSCh and PSMY-Rs) were synthesized from 4-oxo-4-(prop-2-ynyloxy)butanoic acid (PS) (Scheme 1). Polymerizations of the monomers were carried out in tetrahydrofuran (THF) or toluene using rhodium catalyst $[Rh(nbd)Cl]_2$ (Rh**1**) or $(nbd)Rh^{+}[\eta^{6}\text{–}(C_6H_5)B^{-}(C_6H_5)_3$ (Rh**2**) (Scheme 2). Progress of the polymerization was confirmed by ^{1}H NMR spectroscopy. The results of polymerizations of PSCh and PSMY-Rs are summarized in Tables 1 and 2, respectively. The *cis*-contents of polymers were calculated by ^{1}H NMR integration ratios of a *cis* vinyl proton at 6.6–6.2 ppm and $–CH_2–CH_2–$ protons at 2.8–2.0 ppm (Fig. 1) [12], and the calculational results are also summarized in Tables 1 and 2.

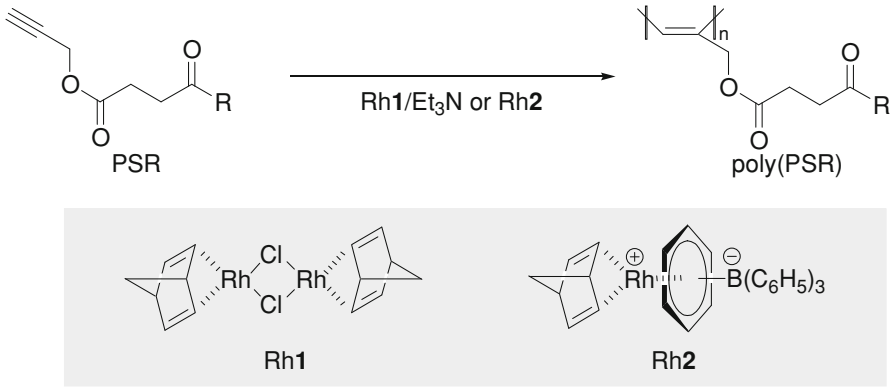
In Table 1, the *cis* contents of poly(PSCh)s were not determined because the methine peak due to olefin in the main chain is very broad. Raising the reaction temperature, yields were slightly increasing but molecular weights of the polymer were not different. GPC curves of these polymers showed bimodal peaks in UV analysis ($M_n = 8000$ and 2500). Polarimetric analysis also showed multi peaks, high molecular part, and middle molecular weight part, but the peak intensity of UV and polarimetric analysis was not proportional relation (Fig. 2). This result suggests that a new chirality in addition to the cholesteryl group was induced in the polymer.



Scheme 1 Syntheses of PSRs

Interestingly, polymerization temperature increasing from 30 to 70 °C, the obtained polymers tended to have negatively high-specific rotation.

Polymerizations of PSMY-Bz were carried out using the rhodium catalysts, Rh**1** and Rh**2**. Using Rh**2** as a catalyst, the polymer yields were higher than those of polymerizations catalyzed by Rh**1** (Table 2). The yields of the polymers obtained from PSMY-Rs in THF were higher than those in toluene, because PSMY-Rs were difficult to dissolve in toluene. These results conformed to our previous work on the polymerization of PSRs [8].



Scheme 2 Polymerizations of PSRs

Table 1 Polymerizations of PSCh ($[\alpha]_{435} = -51.8°$) for 24 h

Run	Solvent (mL)		Temp. (°C)	Yield (%)[a]	$M_n \times 10^{-3}$[b]	M_w/M_n[c]	*cis* content (%)[c]	$[\alpha]_{435}$ (deg.)[d]
1	THF	3	30	35.4	4.8 (8.3,2.4)	1.70	N.D.	N.D.
2	Toluene	3	30	35.3	4.5 (8.0,2.3)	1.94	N.D.	−44.8
3	THF	3	50	46.7	4.4 (8.6,4.4)	1.82	N.D.	−46.9
4	Toluene	3	50	56.7	4.3 (8.7,2.5)	1.81	N.D.	−56.5
5	THF	3	70	46.7	4.2 (7.6,2.4)	1.59	N.D.	−66.1

0.3 g, [PSCh]/[Et_3N]/[Rh**1**] = 100/100/1, *Rh***1** [Rh(nbd)Cl]$_2$

THF tetrahydrofuran, *N.D.* not determined

[a] Methanol-insoluble part

[b] GPC analysis in THF with polystyrene calibration standards

[c] Calculated by ^{1}H NMR integration

[d] $c = 0.1$–1.0 g/dL, $l = 10$ cm

Poly(PSMY-R)s were obtained with moderate molecular weights (M_n = 3100–9300) and relatively narrow polydispersity (M_w/M_n = 1.09–1.56). The *cis* contents of polymers were very low. Even the highest *cis* content, poly(PSMY-PhBz) was obtained in 24% of *cis* content using $CHCl_3$ as a solvent.

The specific rotations of the polymers were negatively larger, compared with those of the monomer. Especially, the largest difference of the specific rotation was observed between the monomer ($[\alpha] = +86.9°$) and the obtained polymer ($[\alpha] = +23.7°$) for liquid crystalline PSMY-PhBz.

Liquid crystalline properties

The mesomorphic phase behaviors of monomers and polymers were characterized by differential scanning calorimetry (DSC) and polarized optical microscopy

Table 2 Polymerizations of PSMY-Rs at 30 °C for 24 h

Run	PSMY-R[a]	Catalyst[b]	Solvent (mL)		Yield (%)[c]	M_n^d	M_w/M_n^d	*cis* content (%)[e]	$[\alpha]_{435}$ (deg.)[f]
1	PSMY-Bz	Rh**1**	THF	4	41.6	6600	1.11	N.D.	N.D.
2		Rh**1**	Toluene	20	35.1	5500	1.16	5.1	+30.4
3		Rh**2**	THF	4	75.2	6800	1.09	7.6	+33.9
4		Rh**2**	Toluene	20	61.0	6700	1.46	N.D.	+36.8
5	PSMY-CNBz	Rh**2**	THF	4	86.8	9300	1.31	21.0	+55.5
6		Rh**2**	Toluene	20	65.6	5100	1.13	N.D.	+63.6
7	PSMY-PhBz	Rh**2**	THF	4	61.4	3100	1.16	N.D.	+24.9
8		Rh**2**	Toluene	20	–	–	–	–	–
9		Rh**2**	$CHCl_3$	4	60.9	5100	1.56	24.0	+23.7

THF tetrahydrofuran

[a] 0.3 g; PSMY-Bz ([α] = + 88.1°), PSMY-CNBz ([α] = + 88.1°), and PSMY-PhBz ([α] = + 86.9°)

[b] [PSR]/[Et_3N]/[Rh**1**] = 100/100/1, Rh**1** [Rh(nbd)Cl]$_2$

[PSR]/[Rh**2**] = 100/1, Rh**2** (nbd)$Rh^+[\eta^6$–(C_6H_5)–$B^-(C_6H_5)_3]$

[c] Diethylether-insoluble part

[d] GPC analysis in THF with polystyrene calibration standards

[e] Calculated by ^{1}H NMR integration

[f] c = 0.1 g/dL, l = 5.0 cn, THF

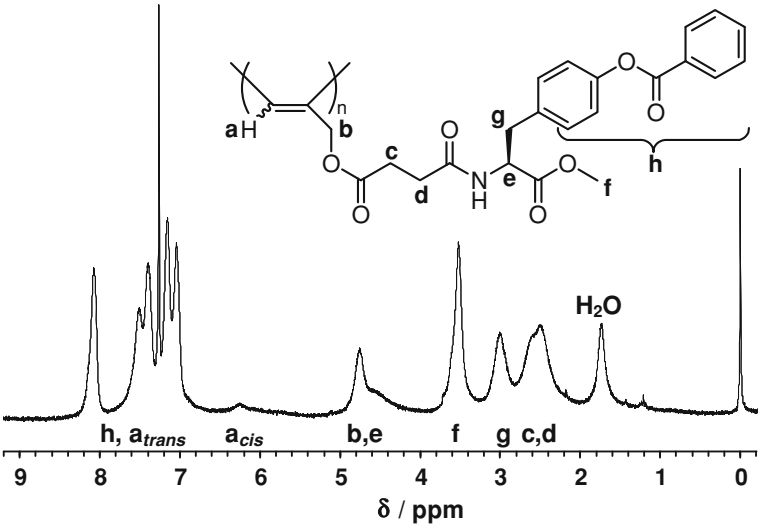


Fig. 1 ^{1}H NMR spectrum of poly(PSMY-Bz) in CDCl3

(POM). All polymers were measured with a heating rate of 10 °C min^{-1}. It is noted that isomerization temperature from *cis* to *trans* form is 150–200 °C [7, 13].

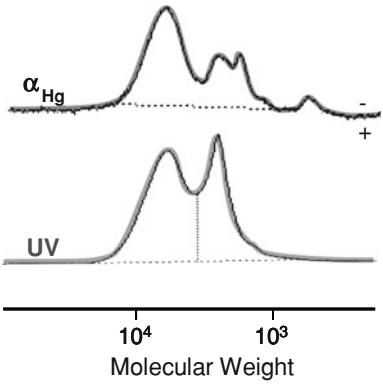


Fig. 2 GPC curves for poly(PSCh); Table 1, Run 3. The top chromatogram was measured by polarimetric detector (αHg) and the bottom by UV detector (254 nm)

Table 3 Thermal characterization of monomers and polymers

Monomer	Phase transition temperature (°C)								Polymer	Run	Phase transition temperature (°C)				
PSCh	C	50	I	81	N*	83	I		poly(PSCh)	Run 1[a]	C	51	N*	170	I
PSMY-Bz	C			33			I		poly (PSMY-Bz)	Run 3[b]	C		–		I
PSMY-CNBz	C			92			I		poly (PSMY-CNBz)	Run 5[b]	C		–		I
PSMY-PhBz	C	87		N	88		I		poly (PSMY-PhBz)	Run 7[b]	C	–	N*	105	I

C crystalline solid, *N** chiral nematic phase, *I* isotropic phase

[a] Run number in Table 1

[b] Run number in Table 2

The corresponding phase transition temperatures and the phases of the synthesized monomers and polymers, obtained during the first cooling, are summarized in Table 3.

The mesomorphic phase behavior during the first cooling scan is summarized in Table 3. Liquid crystalline textures are shown in Fig. 3. DSC curves of PSMY-PhBz and poly(PSMY-PhBz) are shown in Fig. 4. PSCh and poly(PSCh) and PSMY-PhBz exhibited chiral nematic phase (N^*), and PSMY-PhBz especially exhibited the schlieren texture. This difference of PSMY-Rs was probably due to the rigidity of mesogen and the strength of the intermolecular interactions, such as π–π stacking. In addition, poly(PSMY-PhBz) exhibited the nematic phase. The polymer had the highest *cis* contents, 24%. The LC properties of polymers are determined by the stereochemistry of the polymer, especially the double bond configuration. High contents of *cis* double bonds might favor the formation of the more stable and higher-ordered LC phase.

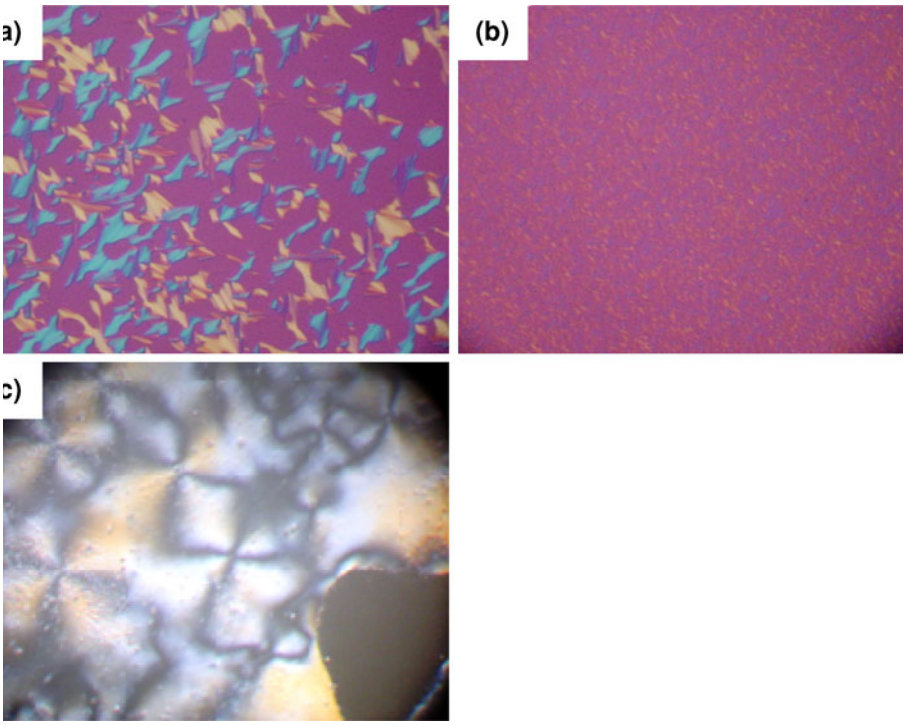


Fig. 3 POM micrographs; **a** PSCh, **b** poly(PSCh), and **c** PSMY-PhBz

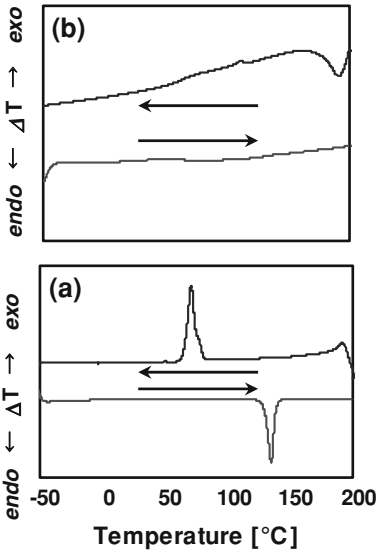


Fig. 4 DSC curves of **a** PSMY-PhBz and **b** poly(PSMY-PhBz)

Conclusion

In this study, we have demonstrated syntheses and polymerizations of chiral PSRs (PSCh and PSMY-Rs) to investigate the effect of the ester bonding on chiroptical and liquid crystal properties of chiral liquid crystalline polyacetylenes. The polymerizations of PSRs were carried out in THF or toluene using $[Rh(nbd)Cl]_2$ and $(nbd)Rh^{+}[\eta^{6}–(C_6H_5)–B^{-}(C_6H_5)_3]$. GPC curves of poly(PSCh)s showed bimodal peaks, and suggests that chirality other than cholesterol was induced in the polymer. PSCh, PSMY-PhBz and these polymers exhibited the chiral nematic phase.

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