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Syntheses and Chirality Control of Optically Active Poly(diphenylacetylene) Derivatives

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ABSTRACT: Optically active poly(diphenylacetylene) derivatives, poly(4-((*S*)-2-methoxyoctyloxy)diphenylacetylene) (**poly-1**), poly(4-((*S*)-2-triethylsiloxyoctyloxy)diphenylacetylene) (**poly-2**), and poly(4-((*S*)-2-hydoxyoctyloxy)diphenylacetylene) (**poly-3**), were successfully synthesized and were examined about their chiroptical and liquid crystalline properties. The mirror image of circular dichroic (CD) spectra of **poly-1** and **poly-2** in dilute solution indicated that their polymer backbones adopted a helical conformation with the opposite handedness. **Poly-3** prepared from **poly-2** by deprotection of a triethylsilyl group showed the same helical handedness with **poly-2**. **Poly-1**−**poly-3** had a lyotropic liquid crystalline property while thermotropic liquid crystalline behavior was observed for **poly-1** and **poly-3**. **Poly-1**−**poly-3** spin-cast films showed a strong bisignate CD signal centered at absorption band of polymer backbone, which suggested the formation of a chiral organization. Thermal annealing enhanced the induced chirality in **poly-3** film and inversed the induced chirality in **poly-1** film. Simple exposure to organic solvent vapor also enhanced the induced chirality in poly-**1**−**poly-3** films. Furthermore, the intensity of induced chirality in **poly-3** film was reversibly controlled by exposing to appropriate solvent vapor alternately.

Introduction

Optically active polymers have been extensively studied aiming at the application in optoelectronic devices and chiral recognition materials including asymmetric catalyst, chiral stationary phase of HPLC, enantioselective permeation membrane, and chiral adsorbent.[1] Recently, chiral assemblies[2] both in solution and in the film have been reported in several synthetic polymers including π-conjugated poly(*p*-phenyleneethnylene)s,[3] poly(*p*-phenylene)s,[4] poly(*p*-phenylenevinylene)s,[5] poly(fluorene)s,[6] poly(thiophene)s,[7] and σ-conjugated poly(silane)s.[8] The polymers in chiral aggregate phase shows extremely large chirality because of the higher order twist of neighboring polymer chains, which is expected to improve the optoelectronic properties and chiral recognition ability. The detailed study of chiral organization by solid CD measurement is necessary for these applications because the chiroptical properties in the film are sensitive to the casting condition and the external stimuli. For example, the sign of induced chirality in the film is controllable by the choice of casting solvent and casting rate.[5c,7c,7d] After the film preparation, thermal annealing at the temperature in thermotropic liquid crystal or in melt can enhance and inverse the induced chirality.[3a,5b,7a,7g,8c]

We previously reported that the simultaneous changes of color and helical conformation[9a] and the inversion of main-chain chirality[9b] of optically active poly(phenylacetylene)s having a OH group could be induced in films by exposing to solvent vapor and/or by heating. This method was expected to control the higher order chiral structure and was useful for controlling the chiroptical properties due to the dynamic helical conformation in the solid thin film. We recently found that lyotropic liquid crystalline monosubstituted poly(acetylene) having an amide group exhibited the characteristic chirality which was induced in film probably due to the formation of a chiral organization.[9c] The sign and intensity of the induced chirality could be controlled by selecting the casting solvent and concentration. Enhancement and inversion of the induced chirality were achieved even after the film preparation by exposing to appropriate solvent vapor though the reversible control could not. Since this polymer showed the lyotropic liquid crystal, the relationship between the induced chirality and the liquid crystalline property in other type of substituted poly(acetylene) should be explored to clarify the generality of the relationship.

Poly(diphenylacetylene) derivatives (PDPA) obtained by group 5 transition metal catalysts have exhibited good thermal stability, photo- and electroluminescence, and high gas permeability in free-standing membrane.[10−12] Some chiral PDPAs showed large CD effects in conjugated main-chain region derived from a helical conformation.[12] The self-standing membrane exhibits remarkable chiral recognition ability in enantioselective permeation to some amino acid and alcohol.[1f,12] It was also reported that PDPAs having an alkylsilyl group showed main-chain type polymer liquid crystal in highly concentrated solution due to their main-chain stiffness.[11] Stiff PDPA with a chiral substituent as well as other planar type chiral conjugated polymers is expected to form a chiral organization, although main-chain type liquid crystalline PDPA having chiral moiety had never been reported.

There are still few examples of chiral PDPA because the polymerization by group 5 transition metals is sensitive to even a weak polar substituent including an *n*-alkoxyl group. Thus, the helical structural study of chiral PDPA having a strong polar group such as amide and OH group had never been reported. However, Tang et al. recently found that disubstituted acetylenes with ether pendant group could be polymerized by WCl_6-Ph_4Sn.[1c,10c] This important finding spreads the variation of pendant group. Hence, with the aim of the formation of chiral organization and liquid crystal, we designed three novel optically active poly(*p*-alkoxydiphenylacetylene) derivatives

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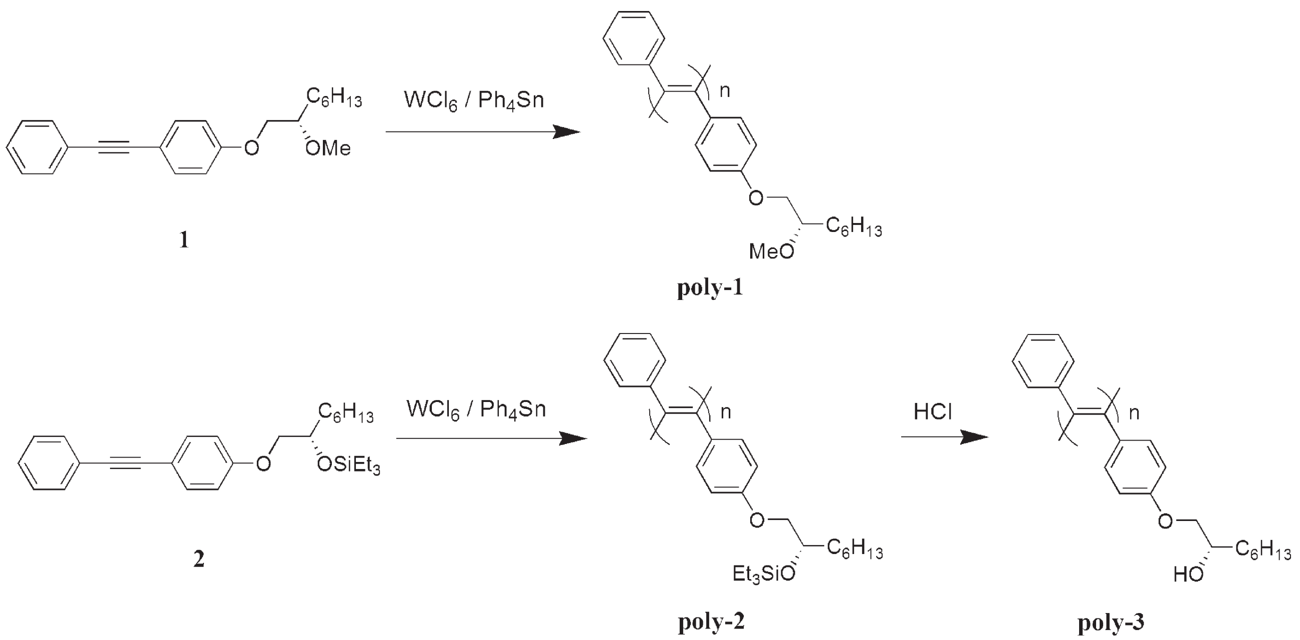
Scheme 1. Synthesis of Optically Active Poly(diphenylacetylene)s



(**poly-1**−**poly-3**) having a chiral methoxy, triethylsiloxy, and OH group, respectively. Herein, the effects of bulkiness and polarity in the side chain on helical conformation in solution and chiroptical properties in the solid and the relationship between liquid crystalline properties and the induced chirality in the film are reported.

Experimental Section

Measurements. NMR spectra were measured on an Avance 400 spectrometer operating at 400 MHz for ^{1}H with TMS as internal standard. Optical rotation was measured on a JASCO P-1020 polarimeter in 10 cm quartz cell at room temperature (ca. 25 °C). CD and absorption spectra were measured on a JASCO J-820 spectoropolarimeter equipped with a temperature controller JASCO PTC-423 L. Gel permeation chromatography (GPC) was performed with using a TOSOH AS-8020 liquid chromatograph equipped with a RI (TOSOH RI-8020) detector and a column oven (TOSOH CO-8020). The molecular weight (M_n) and polydispersity (M_w/M_n) of polymers were determined at 40 °C using three columns (Shodex GPC K-805 L) connected in series, and chloroform was used as eluent at flow rate of 1 mL/min. The molecular weight calibration curve was obtained with polystyrene standards. Microscopic analyses were performed with an Olympus BH-2. Solid thin film was prepared on the surface of 18×18 mm glass plate by spin-coating at 1000 rpm for 5 s and then at 2000 rpm for 5 s using a MIKASA spin-coater 1H-D7.

Monomer Syntheses. (*S*)-1-(4-Iodophenoxy)-2-octanol (**4**) was prepared according to reference to the method of the literature.[13,14] ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H), 1.30−1.34 (m, 8H), 1.49−1.59 (m, 2H), 2.19 (bs, 1H), 3.79 (dd, 1H), 3.93 (dd, 1H), 3.98−4.00 (m, 1H), 6.67−6.71 (m, 2H), 7.54−7.58 (m, 2H).

*4-(2-Hydoxyoctyloxy)diphenylacetylene (**3**).* To a mixture of **4** (4.00 g, 11.5 mmol), bis(triphenylphosphine)palladium dichloride (0.024 g, 0.03 mmol), triphenylphosphine (0.036 g, 0.12 mmol), and copper(I) chloride (0.039 g, 0.18 mmol) in triethylamine (50 mL) was added ethynylbenzene (4.80 g, 13.8 mmol). The reaction mixture was stirred under nitrogen at 40 °C for 2 h. After filtration, the filtrate was evaporated, quantitatively yielding clear oil. This product was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.31−1.35 (m, 8H), 1.50−1.60 (m, 2H), 2.25 (bs, 1H), 3.45 (dd, 1H), 3.98 (dd, 1H), 3.98−4.00 (m, 1H), 6.88−6.90 (d, 2H), 7.29−7.36 (m, 3H), 7.45−7.54 (m, 4H).

*4-(2-Methoxyoctyloxy)diphenylacetylene (**1**).* Sodium hydride (60% dispersion in mineral oil) (0.744 g, 18.6 mmol) was added to a solution of **3** (2.00 g, 6.2 mmol) and iodomethane (21.1 g, 124 mmol) in THF (35 mL) at 0 °C and then stirred at room temperature for 3 h. To the resulting solution was added 40 mL of diethyl ether, washed with a saturated aqueous solution of NH_4Cl, water, and brine, and then dried over $MgSO_4$. After filtration, the filtrate was concentrated in vacuo and purified by column chromatography on silica gel (1:5 EtOAc:*n*-hexane) to provide **1** as a colorless liquid (1.587 g, 76.1% yield); $[\alpha]_D$ −16.7 (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.30 (m, 8H), 1.59−1.62 (m, 2H), 3.48 (s, 3H), 3.54 (m, 1H), 3.98 (d, 2H), 6.88−6.90 (d, 2H), 7.30−7.35 (m, 3H), 7.45−7.52 (m, 4H).

*4-(2-Triethylsiloxyoctyloxy)diphenylacetylene (**2**).* Triethylsilyl chloride (0.841 g, 5.6 mmol) was added to a solution of **3** (1.50 g, 4.6 mmol) and imidazole (0.380 g, 5.6 mmol) in dry CH_2Cl_2 (32 mL) at 0 °C and then stirred at room temperature for 1 h. To the resulting solution was added 40 mL of CH_2Cl_2, washed with water and brine, and then dried over $MgSO_4$. After filtration, the filtrate was concentrated in vacuo and purified by column chromatography on silica gel (1:10 CH_2Cl_2:*n*-hexane) to provide **2** as a colorless liquid (1.506 g, 74.1% yield); $[\alpha]_D$ −36.3 (*c* 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.61−0.67 (m, 6H), 0.80 (t, 3H), 0.91−0.99 (m, 9H), 1.28 (m, 8H), 1.55 (m, 2H), 3.86 (d, 2H), 4.03 (m, 1H), 6.86 (d, 2H), 7.30−7.35 (m, 3H), 7.45−7.52 (m, 4H).

Polymerizations. Polymerization was conducted according to the method of the literature.[1c,10c]

Poly-1. Polymerization of **1** ([M] = 0.5) was carried out under a nitrogen atmosphere with WCl_6-Ph_4Sn ([M]/[W] = 50, $[Ph_4Sn]/[W] = 2.0$) as catalyst in toluene at 60 °C. The reaction mixture was stirred for 24 h, and then the polymer was isolated after precipitation into methanol as a pale yellow powder (81.0% yield); M_n 2.85×10^4, M_w/M_n 1.7, $[\alpha]_D$ +846.2 (*c* 0.10, $CHCl_3$).

Poly-2. A pale yellow powder (44.0% yield); M_n 2.87×10^4, M_w/M_n, 1.7, $[\alpha]_D$ − 781.8 (*c* 0.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.61 (br, 6H, Si−(CH_2−CH_3)$_3$,), 0.91 (br, 12H, −CH_3 and Si−(CH_2−CH_3)$_3$,), 1.29 (br, 8H), 1.45 (br, 2H), 3.58 (br, 2H), 3.90 (br, 1H), 6.05 (br, 2H), 6.60 (br, 2H).

Poly-3. Powdery **poly-2** (0.13 g) was stirred in HCl (5 mL) at room temperature for 24 h. The resulting product was extracted by 30 mL of $CHCl_3$, washed with water twice and brine, and then

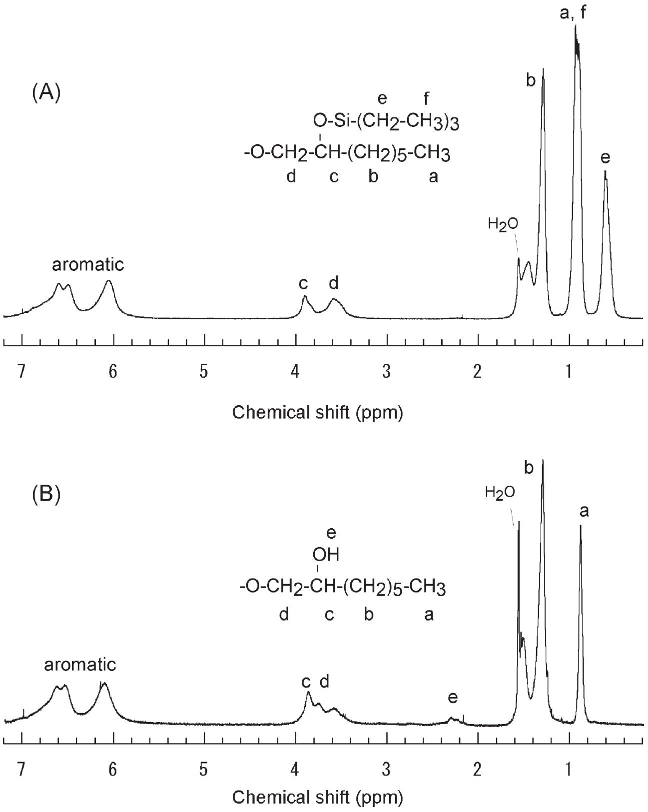


Figure 1. ^{1}H NMR spectra of chloroform-*d* solutions of (A) **poly-2** and (B) **poly-3**.

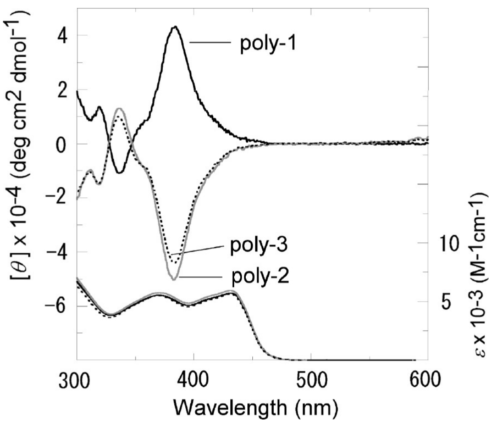


Figure 2. CD and absorption spectra of **poly-1** (black line), **poly-2** (gray line), and **poly-3** (dashed line) measured in $CHCl_3$ (0.25 mM) at ca. 25 °C.

dried over $MgSO_4$. After filtration, the filtrate was concentrated in vacuo to provide **poly-3** quantitatively as a greenish-yellow powder; M_n 2.79 × 10^4, M_w/M_n, 1.9, $[\alpha]_D$ − 967.6 (*c* 0.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.88 (br, 3H, $-CH_3$), 1.30 (br, 8H), 1.52 (br, 2H), 3.58 (br, 1H), 3.88 (br, 2H), 6.13 (br, 2H), 6.54 (br, 2H).

Results and Discussion

Syntheses of Polymers. Polymerization of chiral monomers **1** and **2** by WCl_6-Ph_4Sn afforded yellowish polymers with moderate yield though polymerization by $TaCl_5-Et_3SiH$ did not proceed. The number-average molecular weight (M_n) of **poly-1** and **poly-2** was 2.85 × 10^4 and 2.87 × 10^4, respectively. **Poly-1** having a methoxyl group and **poly-2** carrying a triethylsiloxyl group were soluble in toluene, THF, and $CHCl_3$ and insoluble in acetone, hexane, and methanol. Monomer **3** with a strong polar OH group was not polymerized by WCl_6-Ph_4Sn and $TaCl_5-Et_3SiH$. Accordingly, **poly-3** was obtained from **poly-2** by deprotection of a triethylsilyl group in HCl (Scheme 1). Completion of the reaction was confirmed by vanishing of triethylsilyl peaks in ^{1}H NMR spectra (Figure 1). Since M_n of **poly-3**, 2.79 × 10^4, was similar to that of **poly-2**, no cleavage of polymer chain must occur during the reaction. **Poly-3** was soluble in acetone, toluene, THF, and $CHCl_3$ completely and methanol partly and insoluble in hexane.

Chiroptical Properties in Dilute Solution. The values of specific rotation ($[\alpha]_D$) of **poly-1**, **poly-2**, and **poly-3** were observed as +846.2, −781.8, and −967.6 ($CHCl_3$, *c* 0.10), respectively, which were typical order for helical poly(acetylene) derivatives, while those of monomers **1**, **2**, and **3** were 1 order smaller. The CD and absorption spectra of these polymers were also measured in dilute solution (0.25 mM) in order to estimate the helical structure of backbone (Figure 2). **Poly-1** in $CHCl_3$ showed an apparent positive Cotton effect around 380 nm in the main-chain absorption region. The maximum value of g_{CD}[13] in solution was +0.0026 at 384 nm. This 10^{-3} order value was valid for single helical polymer. These results indicated that polymer backbone adopted a predominantly helical conformation in dilute solution. Since **poly-2** showed the mirror image of the CD spectrum of **poly-1** in $CHCl_3$ solution, the main-chain helicity of these polymers was opposite-handedness to each other. The main-chain helicity was strongly dependent on the bulkiness of chiral group. **Poly-3** in $CHCl_3$ showed the same CD spectrum as that of **poly-2**, which suggested that the helical conformation should remain unchanged after deprotection.

In the CD measurements in toluene at 20 and 100 °C on heating and cooling processes, both **poly-1** and **poly-2** showed the reversible small changes of CD signals whereas irreversible large decrease of the intensity of CD signals was observed for **poly-3** (Figure 3). **Poly-1** and **poly-2** having the bulkier chiral group must adopt more stable helical structure below 100 °C than **poly-3** having a polar OH group. The solvent dependency on helical conformation in solution has been often observed for dynamic helical polymers. However, similar CD spectra of polymers in toluene and $CHCl_3$ showed that the helical conformation was independent of these solvents. As these indications of semiflexible structure of polymer backbone, the main-chain helicity of **poly-1** and **poly-2** was presumably determined during the polymerization process due to the difference of bulkiness of chiral group. The helical conformation of **poly-3** should be derived directly from that of **poly-2**.

Casting Solvent Effect on Film Chirality. **Poly-1** spin-cast film prepared from 2 wt % $CHCl_3$ solution showed a more split and intense CD spectrum than that in the corresponding solution (Figure 4A). The induced CD spectrum consisted of a negative first Cotton effect at 440 nm, a positive second Cotton effect at 405 nm, a negative third Cotton effect at 375 nm, and a negative fourth Cotton effect at 320 nm. The maximum g_{CD} value was +0.021 at 405 nm, which was 8 times larger than that in solution. Kwak et al. already revealed that absorption band around 430 nm of PDPA is due to the $\pi-\pi^*$ transition of conjugated main-chain axis.[11e] Hence, it was considered that the strong CD couplet zero crossing at 433 nm in the film was mainly due to the exciton coupling of neighboring polyene chromophores. The CD couplet centered at main-chain absorption was often observed for conjugated polymers in chiral aggregate phase.[2−8] The handedness of chiral organization could be generally

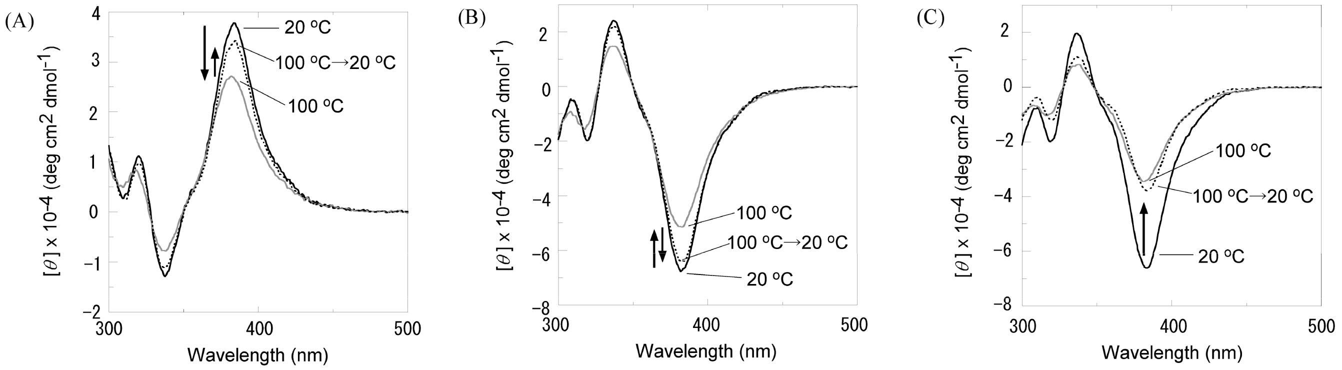


Figure 3. CD spectra of (A) **poly-1**, (B) **poly-2**, and (C) **poly-3** measured in toluene (0.25 mM) at various temperatures.

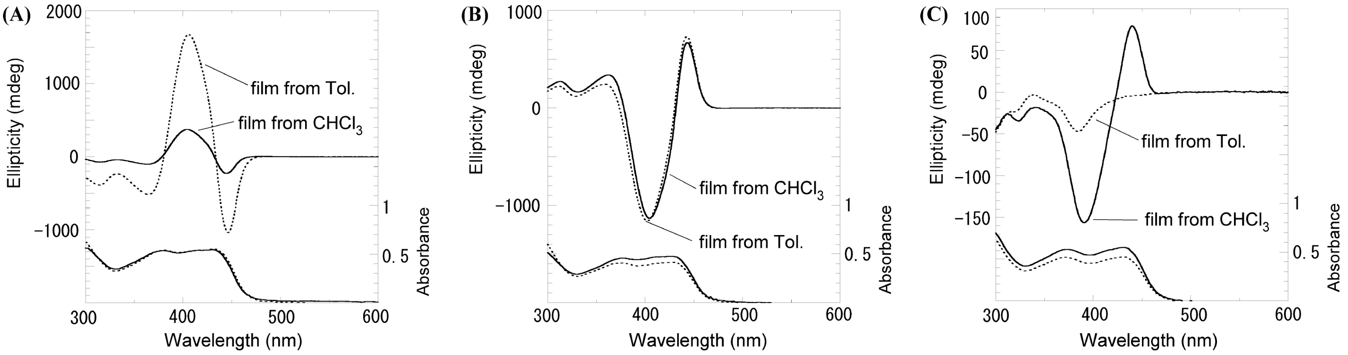
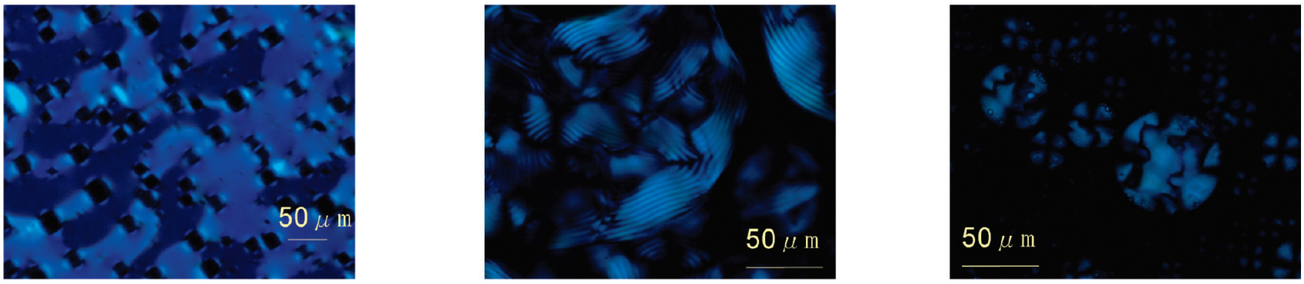
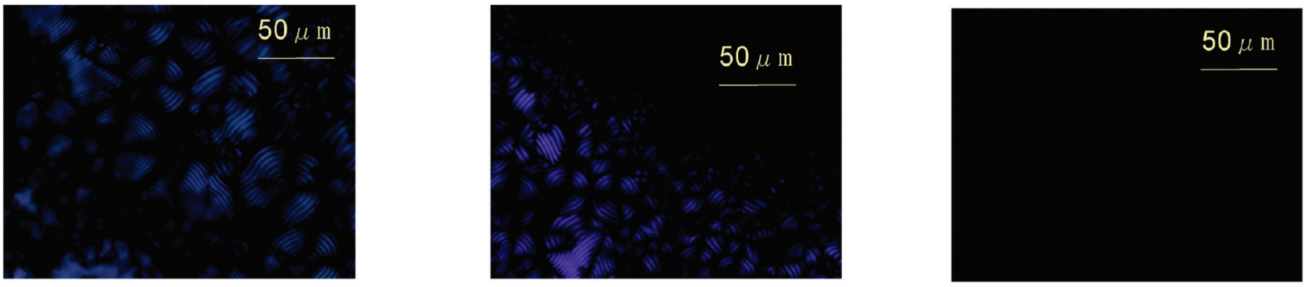


Figure 4. CD and absorption spectra of (A) **poly-1**, (B) **poly-2**, and (C) **poly-3** spin-cast films from 2 wt % $CHCl_3$ (black line) and 4 wt % toluene (dashed line) solution.



poly-1 in 20 wt % $CHCl_3$ **poly-2** in 20 wt % $CHCl_3$ **poly-3** in 30 wt % $CHCl_3$



poly-1 in 12.5 wt % Tol. **poly-2** in 20 wt % Tol. **poly-3** in 25 wt % Tol.

Figure 5. Polarized optical microscopic images of polymers in highly concentrated solution.

determined by the CD exciton chirality method.[15] Thus, the negative CD couplet at 433 nm observed in **poly-1** film from 2 wt % $CHCl_3$ solution suggested the formation of a left-handed chiral organization. **Poly-1** film prepared from 4 wt % toluene solution also exhibited a negative CD couplet at 433 nm. However, the g_{CD} value was $+0.097$ at 405 nm, which was ~5 times larger than that of the film prepared from 2 wt % $CHCl_3$ solution which had similar film thickness. The g_{CD} value in **poly-1** pristine films depended on casting solvent though the sign was the same irrespective of that.

The sign of all Cotton effects in **poly-2** film prepared from 2 wt % $CHCl_3$ solution was fully opposite to that in **poly-1** film (Figure 4B). The maximum g_{CD} value was observed as -0.075 at 405 nm, which was ~30 times larger than that in

Table 1. Solvent Dependency on the Formability of Lyotropic LC and the Value of g_{CD} in the Pristine Films

	lyotropic LC phase		g_{CD} value in the pristine film	
polymer	in toluene (wt %)	in $CHCl_3$ (wt %)	from 4 wt % toluene	from 2 wt % $CHCl_3$
poly-1	cholesteric (12.5)	nematic (20)	+0.097	+0.021
poly-2	cholesteric (20)	cholesteric (20)	−0.075	−0.075
poly-3	−[a] (25)	cholesteric (30)	−0.0026	−0.076

[a] No texture was observed.

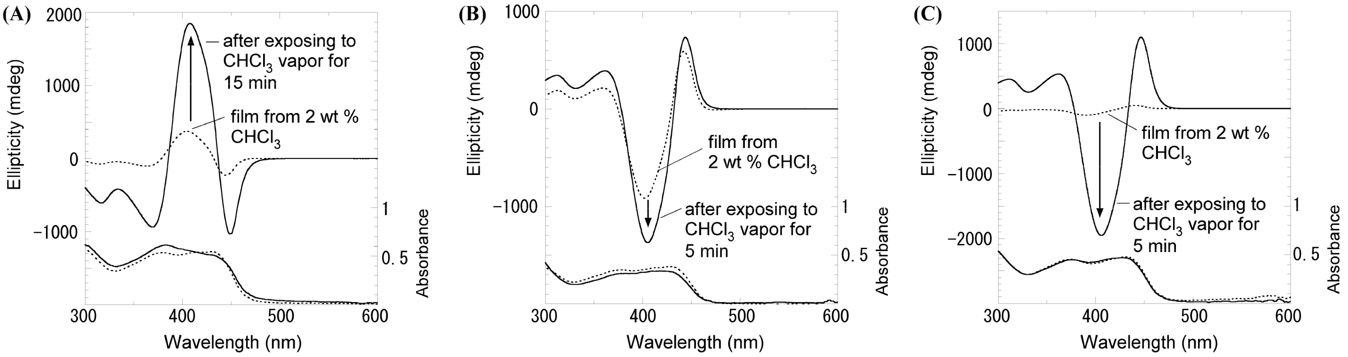


Figure 6. CD and absorption spectra of (A) **poly-1**, (B) **poly-2**, and (C) **poly-3** spin-cast films from 2 wt % $CHCl_3$ solution before (dashed line) and after (solid line) exposing to $CHCl_3$ vapor at ordinary pressure and temperature.

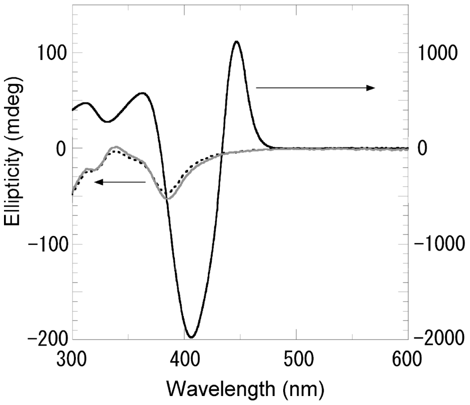


Figure 7. CD spectra of **poly-3** spin-cast film from 4 wt % toluene solution before (left axis, dashed line) and after (right axis, black line) exposing to $CHCl_3$ vapor for 5 min and (left axis, gray line) further exposing to toluene vapor for 5 min at ordinary pressure and temperature.

the corresponding solution. Hence, the positive CD couplet at 430 nm observed in **poly-2** film was due to the formation of a right-handed chiral organization that was opposite handedness to that in **poly-1** film. The induced CD in **poly-1** and **poly-2** films as well as main-chain helicity in solution showed opposite sign. The film prepared from 4 wt % toluene solution exhibited a very similar CD spectrum to that of the film from $CHCl_3$. Different from **poly-1**, the value of g_{CD} in the **poly-2** films was independent of casting solvent.

Poly-3 film prepared from 2 wt % $CHCl_3$ solution showed a weak positive CD couplet at 430 nm (Figure 4C). Since the g_{CD} value of **poly-3** film was observed as −0.0076 at 390 nm and was 1 order smaller than those of **poly-1** and **poly-2** films, the **poly-3** film presumably contained much less chiral organization elements. On the contrary, **poly-3** spin-cast film prepared from 4 wt % toluene solution showed a similar CD spectrum and the g_{CD} value (−0.0026 at 380 nm) as those in the corresponding solution. Hence, the **poly-3** film from toluene probably contained no chiral organization structure. The formation of chiral organization in the **poly-3** films depended strongly on casting solvent.

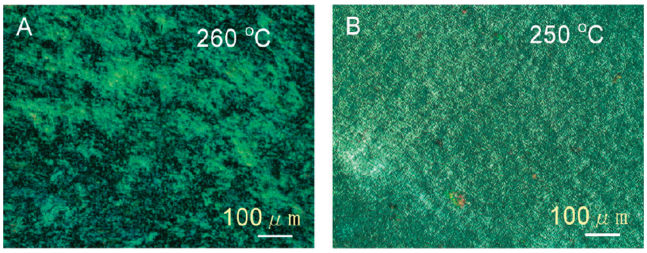


Figure 8. Polarized optical microscopic images of powdery (A) **poly-1** at 260 °C and (B) **poly-3** at 250 °C on first heating process.

Lyotropic Liquid Crystallinity. Poly-1−**poly-3** showed some liquid crystalline textures through polarized optical microscopy (POM) in highly concentrated solution (Figure 5). **Poly-1** formed a cholesteric phase in 12.5 wt % toluene solution, whereas nematic phase was observed in 20 wt % $CHCl_3$ solution. **Poly-2** in both 20 wt % toluene and $CHCl_3$ solutions formed a cholesteric phase. On the contrary, **poly-3** formed a cholesteric phase in 30 wt % $CHCl_3$ solution though no liquid crystalline texture was observed in 25 wt % toluene solution. The formability of liquid crystal in **poly-3** depended strongly on the solvent. The g_{CD} value and the lyotropic liquid crystalline property in various solvents are summarized in Table 1 showing some interrelation. The larger g_{CD} value was observed in the film from the solvent whose formability of cholesteric phase was larger than that of nematic phase. The g_{CD} value was smaller for polymer with lower lyotropic liquid crystallinity. Hence, the chiral organization structure in these films presumably consists of cholesteric liquid crystalline type assembly.

Chirality Control by Solvent Vapor. Thermally control of induced chirality in the film has been reported in several conjugated polymers.[2−8] Thermal annealing in an atmosphere of solvent vapor was previously proposed as another method.[5c] Recently, we found that solvent vapor could irreversibly enhance and inverse the induced chirality in the aliphatic *cis*-poly(acetylene) film even at room temperature.[9c] This facile method is considered to be applicable for other chiral conjugated polymers having lyotropic LC property and has some advantages including restraint of thermal decomposition or

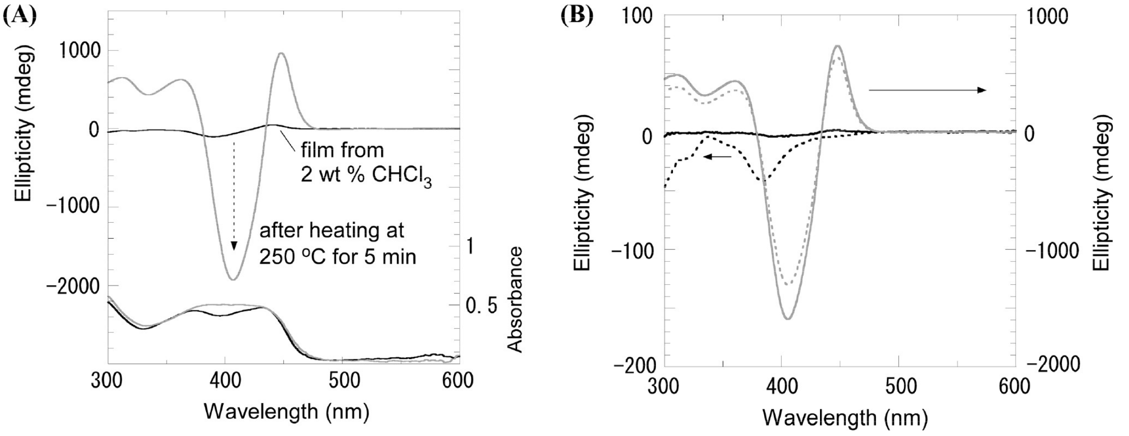


Figure 9. (A) CD and absorption spectra of **poly-3** spin-cast film from 2 wt % $CHCl_3$ solution before (black line) and after (gray line) heating at 250 °C for 5 min. (B) CD spectra of **poly-3** spin-cast film from 4 wt % toluene solution before (left axis, black dashed line) and after (right axis, gray dashed line) heating at 250 °C for 5 min and (left axis, black solid line) further exposing to toluene vapor for 5 min at ordinary pressure and temperature and (right axis, gray solid line) further heating at 250 °C for 5 min. Spectra were measured at ca. 25 °C.

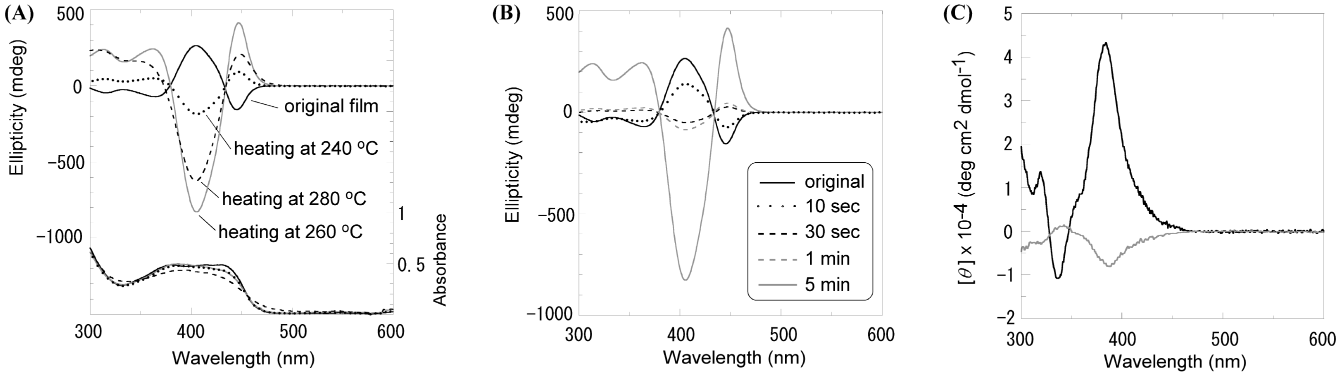


Figure 10. (A) CD and absorption spectra of **poly-1** spin-cast film from 2 wt % $CHCl_3$ solution before (black line) and after heating at 240 °C (dot), 260 °C (gray line), and 280 °C (dashed line) for 5 min. (B) CD spectra of **poly-1** spin-cast film from 2 wt % $CHCl_3$ solution before (black solid line) and after heating at 260 °C for 10 s (dot), 30 s (black dashed line), 1 min (gray dashed line), and 5 min (gray solid line). Spectra were measured at room temperature. (C) CD spectra of **poly-1** measured in $CHCl_3$ solution (0.25 mM) at ca. 25 °C before (black line) and after heating (gray line) whose film at 260 °C for 5 min.

thermal quenching of luminescence. When **poly-1** film from 2 wt % $CHCl_3$ solution, which showed the induced chirality, was exposed to $CHCl_3$ vapor for 15 min at ordinary temperature and pressure and then was dried, all CD signals were enlarged though the absorption spectrum and shape of CD pattern remained unchanged (Figure 6A). The resulting film had kept transparency; therefore, the CD spectrum was reproducible. The g_{CD} value increased dramatically from +0.021 to +0.11 at 405 nm, which suggested that the chiral organization domain should increase in the film due to self-organization of the polymer molecules. This method was also applicable to **poly-2** and **poly-3** (Figure 6B,C). When **poly-2** and **poly-3** films from 2 wt % $CHCl_3$ were exposed to $CHCl_3$ vapor for 5 min, the absolute values of g_{CD} increased from 0.079 to 0.13 at 405 nm and 0.0076 at 390 nm to 0.13 at 406 nm, respectively. Interestingly, the g_{CD} values in **poly-1**−**poly-3** films after contacting with solvent vapor were similar irrespective of the original ones.

Reversible controllability of induced chirality by the solvent vapor method was next examined. When **poly-3** film from 4 wt % toluene was exposed to $CHCl_3$ vapor for 5 min, inducement of a strong positive CD couplet at 430 nm was observed due to novel formation of a predominantly right-handed chiral organization (Figure 7). Further exposure to toluene vapor, in which polymer exhibited no LC, for 5 min reinstated the CD spectral pattern in the pristine film, which suggested the deformation of a chiral organization. The g_{CD} value was reversibly changed between −0.14 at 406 nm and −0.0076 at 390 nm. As mentioned above, **poly-3** formed lyotropic LC in $CHCl_3$, though in toluene no LC phase was observed. Hence, it was revealed that induced CD in the film by solvent vapor could be related to the formability of lyotropic LC. Thus, reversible intensity switching of induced CD was successfully achieved by contacting with two types of solvent vapor, $CHCl_3$ and toluene, by turns. Our versatile method might be applicable to other conjugated polymers having lyotropic LC properties for controlling the induced chirality in the film.

Chirality Control by Thermal Treatment. When **poly-3** film prepared from 2 wt % $CHCl_3$ solution was annealed at 250 °C for 5 min on a hot plate under air, enhancement of a positive CD couplet at 430 nm was observed though the intensity of absorption remained basically the same (Figure 9A). The absolute value of g_{CD} was enlarged from 0.0076 at 390 nm to 0.12 at 407 nm. This suggests that a chiral organization domain increases in the film by thermal annealing. The temperature at which the induced chirality enhanced agreed with the temperature of thermotropic liquid crystal formation (Figure 8). On the contrary, **poly-2** showed no LC phase below 320 °C, and no CD change was observed in annealed film at 200, 240, and 280 °C for 5 min. Since the induced CD spectrum in annealed **poly-3** film was similar to that in the film contacted with solvent vapor, the type of chiral organization was presumably similar in these films. Both solvent vapor exposure and thermal annealing effectively enhanced the induced chirality.

When **poly-3** film from 4 wt % toluene solution which showed no induced CD was annealed at 250 °C for 5 min, a strong positive CD couplet at 430 nm newly appeared (Figure 9B). This indicated that thermal annealing enables polymer molecules to self-assemble to form a predominantly right-handed chiral organization. When this film was exposed to toluene vapor for 5 min, all CD signals almost disappeared, suggesting that not only a chiral organization but also the main-chain helix deformed. When the resulting film that showed no CD was heated at 250 °C for 5 min, a strong positive CD couplet at 430 nm appeared again. This suggested that a right-handed chiral organization should be formed again from the polymer having no main-chain helicity. In planar type conjugated polymers adopting nonhelical conformation, similar inducement of higher order chirality in the film by thermal annealing was reported.[3,5] Hence, it is seen that well-defined main-chain helix should not be necessary for inducing the higher order chiral structure. The chiral substituent in the side chain probably induces the chiral twist of the neighboring polymer chains.

Switching the sign of the induced chirality in the solid state is still challenging topic in area of chiral polymer chemistry. In poly(fluorene) film,[6d] inversion of the induced chirality by thermal annealing was reported. In poly(thiophene)s[7a] and poly(silane)s,[8c] the sign of induced chirality in the films was controllable by adjusting the cooling rate after the thermal annealing. When **poly-1** film prepared from 2 wt % $CHCl_3$ solution was annealed at 240, 260, and 280 °C for 5 min, an inversion of the sign in CD spectra was observed (Figure 10A). The optimal inversion temperature, 260 °C, agreed with the temperature at which apparent birefringence was clearly observed in POM (Figure 8). The inversion of CD couplet at 433 nm suggested the inversion of handedness of chiral organization. The spectral change started within 10 s, and then an inversion of the sign in CD spectrum occurred within 30 s (Figure 10B). The full inversion was finished within 5 min. This rapid inversion implied the higher order helix−helix transition to more thermodynamically favored chiral organization. DSC measurement in the range between 20 and 300 °C on heating rate at 10 °C/min showed no characteristic peak in **poly-1**, which was presumably due to low mobility of the polymer molecule.

There has been few examples about the helical conformation study of polymer chain when the thermal inversion of the induced CD occurred in the films.[6d] In order to investigate the main-chain helicity after the thermal inversion of the induced CD, CD measurement in $CHCl_3$ solution of **poly-1** after heating at 260 °C for 5 min which was satisfied the inversion condition of the induced chirality was conducted. The negative CD signal around 380 nm was observed though the intensity was much weaker (Figure 10C). The main-chain helicity as well as the handedness of chiral organization was suggested to be inversed through thermal annealing. The handedness of chiral organization is seen to be determined mainly by the side-chain chirality rather than main-chain chirality because chiral organization can be formed even from nonhelical **poly-3** having a chiral pendant group. Thermal inversion of chiral organization in the **poly-1** film may be due to the change of chiral side-chain environment caused by inversion of main-chain helicity.

Conclusion

In summary, we succeeded in syntheses of helical poly(diphenylacetylene) derivatives having both thermotropic and lyotropic main-chain type liquid crystalline properties. The large induced CD probably due to a chiral organization was observed in the spin-cast films prepared from solvents in which polymers in highly concentrated solution could form liquid crystal, especially cholesteric phase. Exposure to organic solvent vapor at ordinary temperature and pressure as well as previously described thermal annealing could enable polymers to self-assemble to form a chiral organization. Furthermore, the chiral organization and disorganization in film could be reversibly controlled by alternately exposing to vapor of solvents with and without lyotropic liquid crystal formability. The relationship between the lyotropic liquid crystalline property and the formability of chiral organization was somewhat revealed. Thermal annealing could control the handedness of chiral organization in **poly-1** film and could induce and increase the chiral organization domain in **poly-3** though their main-chain helicity almost deformed. Thus, the solvent vapor method could be recommended for preparing chiral organization in the film from well-defined helical polymer.

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