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Color and Chiroptical Control of Poly(phenylacetylene) Films with Chiral Hydroxyl Group

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ABSTRACT: The effect of the alkyl side chain on the chiroptical properties of optically active poly(4-(2-hydroxyalkoxyl)phenylacetylene) (poly(**1**) and poly(**2**)) and poly(4-(1-hydroxyalkyl)phenylacetylene) (poly(**3**), poly((*S*)-**4**), and poly((*R*)-**4**)) films was examined. Poly(**1**) film showed a reversible color change between yellow and red along with change of circular dichroism (CD) by exposure to solvent vapor and/or by heating, while red poly(**2**) that had a longer alkoxyl group was not color-changeable. Poly(**3**) and poly(**4**) films showed the reversible inversion of the CD spectra, which was completed within several minutes, by exposure to organic solvent vapor and by heating. The CD inversion at lower temperature was observed for poly((*S*)-**4**) and poly((*R*)-**4**) with a longer alkyl chain. Lyotropic liquid crystalline poly((*S*)-**4**) and poly((*R*)-**4**) exhibited the highly induced CD and helical fibril structures in the film by selecting the casting solvent, indicating the formation of a predominantly chiral organization.

Introduction

Chiral conjugated polymer has several intriguing properties and is expected for the potential application such as sensor, chiroptical switch and memory, display device, chiral stationary phase in HPLC, enantioselective separation membrane, and asymmetric catalyst.[1] Control of chiroptical properties in the film has been attracted because of the importance for improvement in optoelectronic devices and chiral recognition materials.

Well-defined *cis*-stereoregular poly(acetylene) derivatives obtained with a Rh complex catalyst have been extensively studied for the past few decades.[1a−j,2] Helical poly(acetylene)s with an excess of one-handedness have been obtained from both chiral monomer,[1a,3] and achiral monomer with chiral cocatalyst.[4] *cis*-Poly(acetylene)s in solution show interesting chiroptical changes due to dynamic helical main-chain structure, which includes color change[5] and inversion of main-chain helicity by external stimuli such as solvent,[6] temperature,[6] and additives.[7]

In the solid phase, *cis*-poly(acetylene)s also exhibit some unique chiroptical properties.[8] It was reported that the color of powdery poly(*p*-alkoxyphenylacetylene)s changes from yellow to black or red by contacting with organic solvent[9] or by compression.[10] However, the color of the powder is derived not only from molecule itself but also from surface structure. Therefore, in order to estimate the color due to the conjugation of molecules itself, measurement of transmitted spectrum of the film is required. We previously reported the color-changeable films of poly(phenylacetylene)s with an achiral substituent such as a relatively long alkyl, alkoxyl, and 2-hydroxyethoxy at the para position, whose transmitted color changed from yellow to orange or red by heating or by contacting with organic solvent vapor.[11] Moreover, circular dichroic (CD) spectra of optically active poly(4-((*S*)-2-hydroxyhexyloxy)phenylacetylene) in the film revealed that the original helical conformation changed along with the color change from yellow to red.[12a] However, reversible color control after the film preparation had never been achieved.

As another interesting study in the solid, the detailed structure of helical *cis*-poly(phenylacetylene) on highly oriented pyrolytic graphite (HOPG) was reported by Yashima et al. through atomic force microscopy (AFM) with X-ray diffraction (XRD) measurement.[13] The helical bundle structure could be inversed by exposure to solvent vapor for several hours, though the inversion was irreversible. There have been some examples of thermodynamically control of the helical main-chain structure even in the solid state. For example, thermal helix inversion has been reported for polypeptides,[14] polyisocyanides,[15] and polysilanes.[16a,b] We recently reported the rapid and reversible chirality inversion of poly(*p*-alkylphenylacetylene) spin-cast film on glass substrate by exposure to solvent vapor or by heating,[12b] although the reason for the rapidity had been unclear.

Chiral assemblies,[1j−l] both in solution and in the solid films, has been found for some conjugated polymers such as poly(*p*-phenyleneethnylene)s,[17] poly(*p*-phenylenevinylene)s,[18] poly(fluorene)s,[19] poly(thiophene)s,[20] and poly(silane)s.[16c,d] *cis*-Poly(acetylene)s with an amide group in the side chain were reported to possess helical conformation with long persistent length stabilized by the intramolecular hydrogen bonding[21] and to form main-chain-type liquid crystals in highly concentrated solution.[22] We recently found that both aliphatic chiral poly(acetylene)s with an amide group and chiral poly(diphenylacetylene)s with an OH group, both of which had lyotropic liquid crystallinity, showed the highly induced CD spectra in the films probably due to the formation of predominantly chiral organization.[12c,d] Furthermore, the intensity and sign of the highly induced CD in the films could be controlled by heating, solvent vapor, or the casting condition. As far as we know, the chiroptical study of chiral organization structure of poly(phenylacetylene) in film had never been reported.

In this paper, the substituent effect of optically active poly(acetylene)s with a chiral OH group on color and chirality change by heating and by solvent vapor in film is examined by using CD spectroscopy, polarized UV−vis spectroscopy, polarized optical microscopy (POM), wide-angle X-ray diffraction (WAXRD), and scanning electron microscopy (SEM). Poly(phenylacetylene)s carrying an alkoxyl group show the reversible and simultaneous change of color and chirality, whereas those having an alkyl group show the reversible inversion of helical chirality. The effect of alkyl

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side-chain length on their chiroptical properties is also studied. Furthermore, the highly induced chirality is controlled by selecting the casting condition and external stimuli.

Experimental Section

General Methods. NMR spectra were measured on a B9-JEOL spectrometer operating at 270 MHz for ^1H with TMS as internal standard. Specific rotation was measured on a JASCO P-1020 polarimeter in a 10 cm quartz cell. Absorption and CD spectra were measured on a JASCO J-820 spectoropolarimeter equipped with a JASCO PTC-423 L temperature controller. Polarized absorption spectra were measured on a JASCO V-570 spectrophotometer. Gel-permeation chromatography (GPC) was performed with using a TOSOH AS-8020 liquid chromatograph equipped with a refractive-index (RI) detector (TOSOH RI-8020) and a column oven (TOSOH CO-8020). The molecular weight (M_n) and polydispersity (M_w/M_n) of poly(**1**) were determined at 40 °C using two TOSOH TSK α-M GPC columns connected in series, and DMF containing 10 mM LiCl was used as eluent at flow rate of 0.5 mL/min. Those values of the other polymers were determined at 40 °C using three Shodex GPC K-805 L columns 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. WAXRD patterns were recorded by a Rigaku ULTRAX 18SF instrument at room temperature using Ni-filtered Cu Kα radiation. Laser Raman spectra were run on a JASCO NRS-2100 instrument. Microscopic analyses were performed with an Olympus BH-2 instrument. The SEM images were recorded on a Philips XL30 ESEM-FEG scanning electronic microscope using an accelerating voltage of 10 kV. The solid thin films were prepared by spin-casting on the surface of 15 × 15 mm glass plate or elastic substrate at 1000 rpm for 5 s and then 2000 rpm for 5 s using a Mikasa 1H-D7 spin-coater.

Scheme 1. Chemical Structures of Poly(phenylacetylene)s with a Chiral Hydroxyl Group

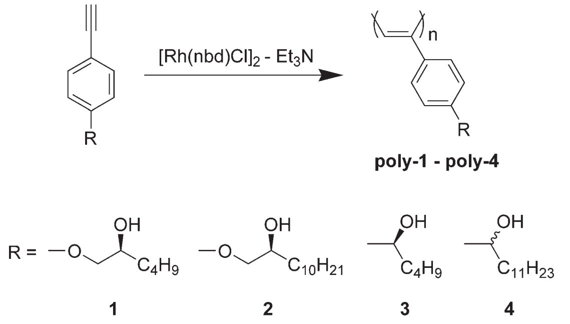

Table 1. Syntheses and Characterization Data of Polymers

run	monomer[a]	yield[b] (%)	M_n[c] (10^4)	M_w/M_n[c]	$[\alpha]_D$[d] (deg)
1	**1**	77	5.7	2.5	+612 (Et_2NH)
2	**2**	83	–[e]	–[e]	–[e]
3	**3**	60	8.1	2.2	+927 ($CHCl_3$)
4	(*S*)-**4**	68	8.1	2.0	+740 ($CHCl_3$)
5	(*R*)-**4**	61	7.9	2.7	−695 ($CHCl_3$)

[a] Polymerization conditions: [M] = 0.2 M, [Rh]/[M] = 0.05, [Et_3N]/[Rh] = 10.0. [b] *c*-Hexane-insoluble part (runs 1 and 3), methanol-insoluble part (runs 2, 4, and 5). [c] Determined by GPC with polystyrene standard. [d] c = 0.1 g/dL, l = 10 cm. [e] Insufficient solubility for measurements.

Materials. All the solvents and the reagents were used as received without further purification. [Rh(norbornadiene)Cl]$_2$ was purchased from Aldrich.

Syntheses of Monomers. (*S*)-1-(4-Ethynylphenoxy)-2-dodecanol ((*S*)-**2**) was prepared from 1,2-epoxydodecane and 4-iodophenol as the starting materials with the similar method to (*S*)-**1**.[12a,23a,b] $[\alpha]_D^{25}$ +12.8 (c 1.00, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ 0.88(t, 3H), 1.24−1.30 (m, 16H), 1.49−1.59 (m, 2H), 2.22 (bs, 1H), 3.00 (s, 1H) 3.83 (dd, 1H), 3.96 (dd, 1H), 3.98−4.02 (br, 1H), 6.83−6.87 (m, 2H), 7.41−7.45 (m, 2H).

(*R*)-1-(4-Ethynylphenyl)-1-dodecanol ((*R*)-**4**) and (*S*)-1-(4-ethynylphenyl)-1-dodecanol ((*S*)-**4**) were prepared from 1-(4-bromophenyl)dodecan-1-one as the starting material, (+)-(1*S*)-B-chlorodiisopinocampheylborane, and (−)-(1*R*)-B-chlorodiisopinocampheylborane with reference to the previously described methods of (*S*)-**3**.[12b,23c] (*R*)-**4**: $[\alpha]_D^{25}$ +16.8 (c 1.00, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ 0.88 (t, 3H), 1.24 (m, 18H), 1.67−1.77 (m, 2H), 3.06 (s, 1H), 4.64−4.68 (m, 1H), 7.30 (m, 2H), 7.47 (m, 2H). (*S*)-**4**: $[\alpha]_D^{25}$ −17.2 (c 1.00, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ 0.88 (t, 3H), 1.24 (m, 18H), 1.67−1.77 (m, 2H), 3.06 (s, 1H), 4.63−4.70 (m, 1H), 7.30 (m, 2H), 7.47 (m, 2H).

Polymerization. Polymerization was carried out in a Schlenk tube equipped with a three-way stopcock under a nitrogen atmosphere with [Rh(norbornadiene)Cl]$_2$ as a catalyst at room temperature for 0.5 h.[2] The detailed polymerization conditions are indicated in Table 1.

Results and Discussion

Polymer Properties. Polymerization of all monomers with Rh catalyst affords yellow or red fibrous polymers with moderate yield. A substituent on the para position hardly affected the polymer yield. Specific rotation ($[\alpha]_D$) of poly(**1**), poly(**3**), poly((*S*)-**4**), and poly((*R*)-**4**) was +612 in Et_2NH, +927 in $CHCl_3$, +740 in $CHCl_3$, and −695 in $CHCl_3$, respectively, while those of the corresponding monomers were one order smaller, indicating that the large $[\alpha]_D$ of polymers in dilute solution was probably due to the main-chain helix with an excess of one-handedness. The opposite sign of $[\alpha]_D$ of poly((*S*)-**4**) and poly((*R*)-**4**) suggested that their helical conformation have opposite handedness. Solubility of the polymers is summarized in Table 2. Yellow poly(**1**) was soluble in highly polar solvents like Et_2NH, DMF, and DMSO, while red poly(**2**) was insoluble in common organic solvents. In contrast with the lower solubility of poly(*p*-alkoxylphenylacetylene)s (poly(**1**) and poly(**2**)), yellow poly(*p*-alkylphenylacetylene)s (poly(**3**) and poly(**4**)) were highly soluble in various organic solvents. Thus, the solubility of the polymers with an alkoxyl group was much lower than those with an alkyl group.

Control of Color and Helical Conformation. Poly(**1**) film exhibited the simultaneous change of color and helical conformation by contacting with a vapor of organic solvents such as acetone, MeOH, THF, $CHCl_3$, and toluene in which polymer was insoluble.[12a] The CD spectrum of the spin-cast film on glass substrate from 4 wt % Et_2NH solution, which consisted of a negative first Cotton effect at 441 nm, a second positive one at 381 nm, and a negative third one at 328 nm,

Table 2. Solubility of Polymers[a]

	n-hexane	*c*-hexane	toluene	$CHCl_3$	THF	acetone	MeOH	Et_2NH	DMF	DMSO
poly(**1**)	−	−	−	−	−	−	−	+	+	+
poly(**2**)	−	−	−	−	−	−	−	−	−	−
poly(**3**)	−	−	−	+	+	+	+	+	+	+
poly((*S*)-**4**)	−	+	+	+	+	−	−	+	+	+

[a] −: insoluble; +: soluble.

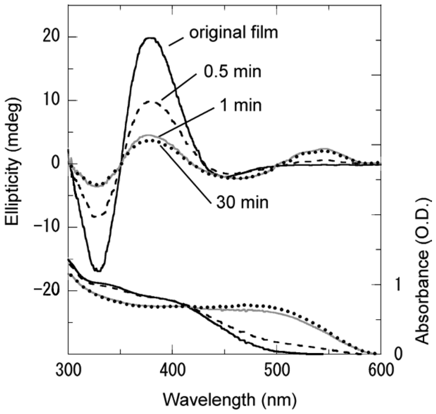

Figure 1. CD (top, left axis) and absorption (bottom, right axis) spectra of poly(**1**) spin-cast film from 4 wt % Et_2NH solution before (black solid line) and after exposure to acetone vapor at room temperature for 0.5 (dashed line), 1 (gray solid line), and 30 min (dot).

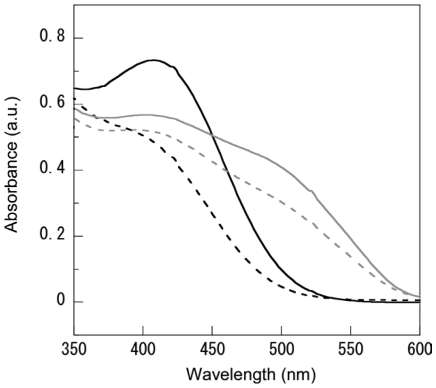

Figure 2. Polarized absorption spectra of poly(**1**) draw films on elastic substrate for 1.3 times before (black line) and after (gray line) exposure to acetone vapor for 1 min. Angles between polarized and drawing direction are 0° (solid line) and 90° (dashed line).

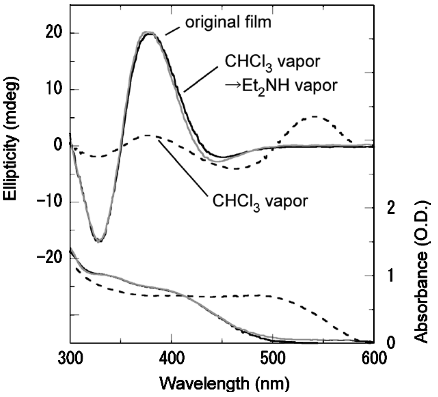

Figure 3. CD (top, left axis) and absorption (bottom, right axis) spectra of poly(**1**) spin-cast film from 4 wt % Et_2NH solution before (black solid line) and after exposure to $CHCl_3$ vapor for 30 min (dashed line) and then further exposure to Et_2NH vapor for 1 min (gray solid line) at room temperature.

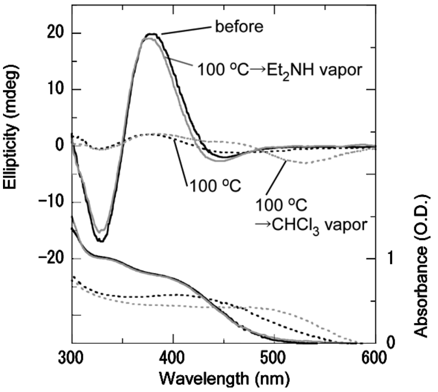

Figure 4. CD (top, left axis) and absorption (bottom, right axis) spectra of poly(**1**) spin-cast film from 4 wt % Et_2NH solution before (black solid line) and after heating at 100 °C for 3 min (black dashed line) and then further exposure to $CHCl_3$ vapor for 30 min (gray dashed line) and Et_2NH vapor for 1 min (gray solid line) at room temperature.

was similar in pattern to that in the corresponding Et_2NH solution. Thus, polymer molecule in the pristine film takes a predominantly helical conformation basically the same as in solution. When the film was exposed to acetone vapor at ordinary temperature and pressure, color change from yellow to red was observed, indicating that the elongation of π-conjugation occurred. This red color remained even after the film was completely dried. Both absorption at around 350 nm and CD signals at 381 and 328 nm became weaker with the color change, and novel appearances of both absorption at around 490 nm and a positive CD signal at 550 nm were observed (Figure 1). It was confirmed that these spectral changes were started within 0.5 min and were almost saturated around 1 min. Little changes of the spectra were observed with further exposure. Similar spectral changes were observed by using MeOH, THF, and $CHCl_3$. The absorption band of 410 nm in the pristine film was mainly attributable to the $\pi-\pi^*$ transition of the main-chain axis because in poly(**1**) stretched film, in which the polymer main chains aligned parallel to the stretching direction, absorption at 410 nm for polarizer angle of 0° was stronger than that for 90° (Figure 2). The novel absorption at around 490 nm, which appeared after exposure to acetone vapor, was also parallel to the main-chain axis, indicating that the orientation almost remained in the color changed film. Hence, it was revealed that π-conjugation mainly elongated in the direction of main-chain axis. The large decrease of CD effects at 381 and 328 nm suggested that original helical conformation should be almost deformed. The novel appearance of a positive CD at 550 nm was probably due to the chiral structure of the elongated main chain.

Reversibility of color change by solvent vapor was examined. When poly(**1**) film from 4 wt % Et_2NH solution was exposed to $CHCl_3$ vapor for 30 min, decrease of both the CD signals at 381 and 328 nm and absorption at around 350 nm and novel appearance of both a positive CD signal at 550 nm and absorption at 490 nm were observed (Figure 3). As mentioned below, the highly ordered alignment of polymer molecules along with the color change was confirmed by WAXRD (Figure 7). This implied that the polymer adopted nearly linear backbone structure rather than random-coil or wormlike structure. When the red film obtained by $CHCl_3$ vapor was further exposed to Et_2NH vapor for 1 min, the color of the film returned to yellow, and the CD and absorption spectra were returned completely to those of the pristine film. The morphology of the film after exposure to Et_2NH vapor returned to amorphous, which was confirmed by XRD as no sharp peak. Thus, color and morphology as well as chirality of the film were reversibly changed and were easily controllable by solvent vapor. These results suggested that this color change should be induced by self-assembly of the polymer molecules.

When poly(**1**) film from 4 wt % Et_2NH solution was annealed at 100 °C for 3 min, a color change from yellow to orange occurred. No color change was observed when this

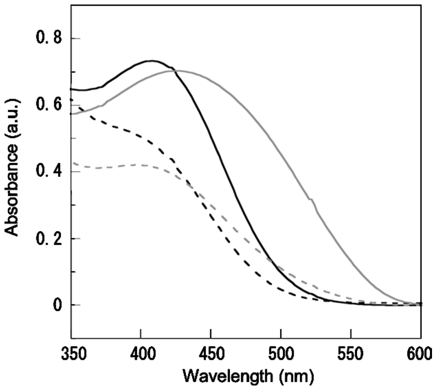

Figure 5. Polarized absorption spectra of poly(**1**) draw films on elastic substrate before (black line) and after (gray line) heating at 100 °C for 3 min. Angles between polarized and drawing direction are 0° (solid line) and 90° (dashed line).

orange film was cooled to room temperature. In the CD spectrum, all CD signals decreased by heating along with increase of absorption at around 450 nm, though no CD signal at longer wavelength appeared (Figure 4). The results of polarized absorption spectra revealed that the novel absorption at around 450 nm was parallel to the main-chain axis, indicating that the π-conjugation elongated mainly in the direction of main-chain axis (Figure 5). A sharp XRD peak appeared at $2\theta = 3.53°$ in the color-changed film, indicating that the polymer molecules oriented with a *d*-spacing of 2.50 nm. No *cis*−*trans* isomerization of main chain occurred that was confirmed by laser Raman spectroscopy.[12a] These results suggest that the polymer molecule in the orange film should possess nonhelical, linearly elongated backbone structure. When this orange film was further exposed to Et_2NH vapor for 1 min, the CD and absorption spectra and morphology were returned completely to those of pristine film. It was reported for some *cis*-poly(acetylene)s that thermal reduction of helical conformation in solution and bulk was accompanied by *cis*−*trans* isomerization and irreversible intramolecular 6π-cyclization followed by chain cleavage.[24] However, the thermally induced color change in our case should not be due to the isomerization and the cyclization of main chain because of its reversibility. When the film after heating at 100 °C was further exposed to $CHCl_3$ vapor for 30 min, the novel appearance of a negative CD signal at 550 nm and an increase of absorption at around 490 nm were observed. Interestingly, the novel CD signal at 550 nm had opposite sign to that of the film after exposure to $CHCl_3$ vapor *without* preheating. By this method, the sign of the novel CD appeared at longer wavelength was controllable.

When poly(**1**) film from 4 wt % Et_2NH solution was exposed to toluene vapor, all CD signals decreased along with an increase of absorption at 469 nm which was different from that induced by acetone, MeOH, THF, and $CHCl_3$ vapor (Figure 6). λ_{max} of novel absorption depended on the kind of solvent. The novel CD signal around 550 nm did not appear as well as the film after heating. The highly ordered alignment of polymer molecules along with the color change was also confirmed by XRD. These results suggest that the polymer in the film obtained by toluene vapor should take nonhelical, linear backbone structure. Yashima et al. revealed by AFM observation that first layer of 11 unit/5 turn helix of *cis*-poly(phenylacetylene) adsorbed on HOPG was transformed to planar zigzag structure.[13] This may support our assumption that helical conformation is able to change to linear structure without isomerization through external stimuli.

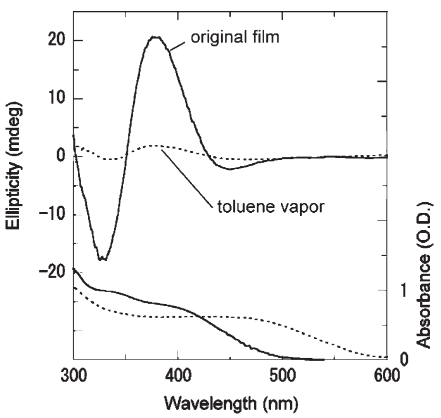

Figure 6. CD (top, left axis) and absorption (bottom, right axis) spectra of poly(**1**) spin-cast film from 4 wt % Et_2NH solution before (solid line) and after exposure to toluene (dashed line) vapor at room temperature for 30 min.

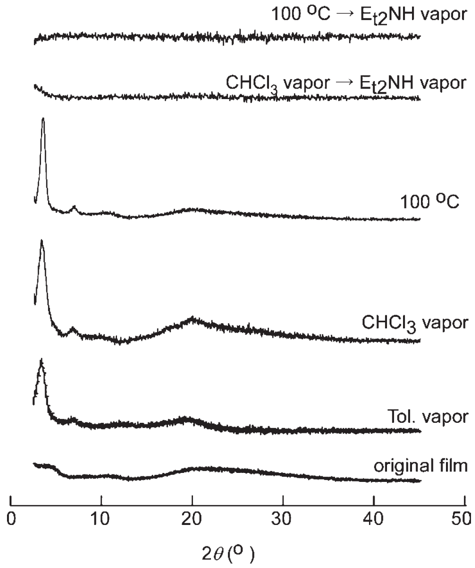

Figure 7. WAXRD patterns of poly(**1**) film before and after exposure to toluene and $CHCl_3$ vapor at room temperature for 30 min and after heating at 100 °C for 3 min and then further exposure to Et_2NH vapor at room temperature for 1 min.

CD Inversion. As mentioned above, among the poly(phenylacetylene)s having a chiral OH group, the polymers with an alkoxyl group at the para position showed simultaneous color and CD change by external stimuli, though CD inversion was not achieved. Thus, we synthesized poly(phenylacetylene) with an alkyl group (poly(**3**)) which showed rapid, reversible, and repeatable CD inversion in the film by exposure to appropriate solvent vapor.[12b] When the spin-cast film of poly(**3**) from 4 wt % Et_2NH solution was exposed to acetone vapor at ordinary temperature and pressure followed by drying, full inversion of the CD spectrum was observed (Figure 8). Inversion immediately occurred and was finished within 1 min. Further exposure to MeOH vapor could reverse the CD spectrum again, and the spectrum showed good agreement with the original one. This reversible inversion was repeatable by alternating exposure to acetone and Et_2NH vapor. The similar CD inversion phenomena have been observed for chiral *cis*-poly(phenylacetylene)s in solution depending on the kind of solvent and have been explained as the inversion of the helical screw sense.[6] Therefore, this CD inversion in the film

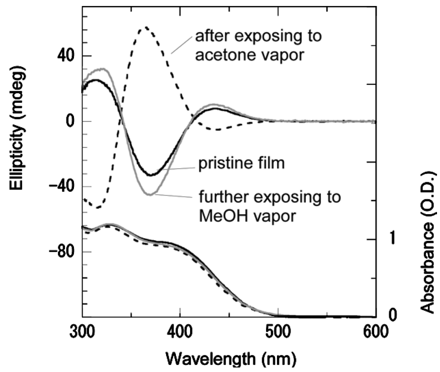

Figure 8. CD (top, left axis) and absorption (bottom, right axis) spectra of poly(**3**) spin-cast film from 4 wt % Et_2NH solution before (black solid line) and after exposure to acetone vapor (black dashed line) and then exposure to MeOH vapor (gray line) for 1 min at ordinary pressure and temperature.

Table 3. Value of g_{CD} at 370 nm of Polymer Films from 4 wt % Et_2NH Solution before and after Exposure to Solvent Vapor for 1 min

	g_{CD} (10^{-3})					
polymer	before	toluene	$CHCl_3$	acetone	MeOH	Et_2NH
poly(**3**)	-0.95^a	+0.98	+1.87	+1.71	−1.39	−1.23
poly((*S*)-**4**)	−1.15	+2.88	+2.63	+1.35	+2.66	−1.75

[a] Exceptional exposure for 3 h.

should be due to the helical inversion, and polymer chain in the film as well as in solution takes a stable helical conformation even after the removal of the solvent. Similar inversion phenomena were also observed for poly(*p*-alkylphenylacetylene) poly(**4**) with a longer dodecyl group. The g_{CD} values[25] of these films before and after exposure to various solvent vapors are summarized in Table 3. The sign and value of g_{CD} were reversibly and repeatedly controlled by exposure to an appropriate solvent vapor for 1 min. However, it took exceptionally 3 h to finish CD inversion of poly(**3**) by vapor of toluene in which polymer did not dissolve. On the other hand, the CD inversion of poly((*S*)-**4**) film was finished within 1 min even by acetone vapor, which is poor solvent (Figure 9). It should be noted that the rapid inversion occurred even by poor solvent in poly((*S*)-**4**) with a longer alkyl side chain.

Thermal inversion of the CD spectrum of poly(**3**) spin-cast film was reported.[12b] To examine the effect of alky chain length on the inversion temperature, CD measurements of poly(**3**) with a pentyl group and poly((*S*)-**4**) with a longer dodecyl group after heating at various temperatures for 1 min were conducted. The full inversion of the CD spectrum in poly(**3**) film from 4 wt % Et_2NH was observed at 110 °C (Figure 10A). On the contrary, poly((*S*)-**4**) film from 4 wt % Et_2NH showed a full CD inversion at 65 °C (Figure 10B). The inversed spectrum in the film remained the same even after cooling to 20 °C. Longer alkyl side-chain could decrease the temperature for CD inversion, probably due to the higher mobility of the polymer molecule. Thus, inversion temperature was controllable by selecting the alkyl side-chain length. When the CD inversed poly(**3**) film that was obtained by heating at 110 °C was further exposed to Et_2NH or MeOH vapor for 1 min, CD reversion occurred again. Similar reversion was also observed for poly((*S*)-**4**) film upon exposure to Et_2NH vapor for 1 min. Neither crystallization nor *cis*−*trans* isomerization took place during both the heating and solvent exposure processes, which were confirmed by WAXRD and by laser Raman spectroscopy.[12b]

Oriented film was studied to clarify the mechanism of CD inversion. If poly((*S*)-**4**) spin-cast film was fabricated on elastic substrate from 4 wt % Et_2NH solution and stretched for 1.5 times, absorption in stretching direction was much stronger than that in perpendicular direction. This indicates that absorption band at 420 nm is mainly derived from π-conjugation of main-chain axis because polymer chains oriented toward stretching direction (Figure 11). After exposure to acetone vapor or annealing at 65 °C for 1 min, which were sufficient condition for CD inversion, the film kept the orientation. This result suggested that the position

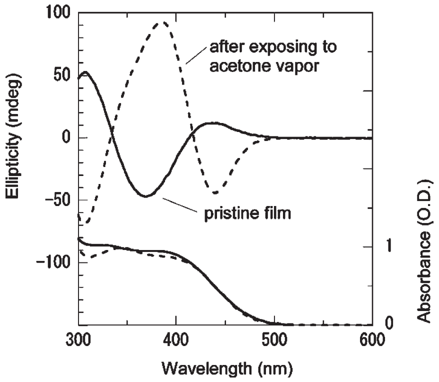

Figure 9. CD (top, left axis) and absorption (bottom, right axis) spectra of poly((*S*)-**4**) spin-cast film from 4 wt % Et_2NH solution before (solid line) and after exposure to acetone vapor (dashed line) for 1 min at ordinary pressure and temperature.

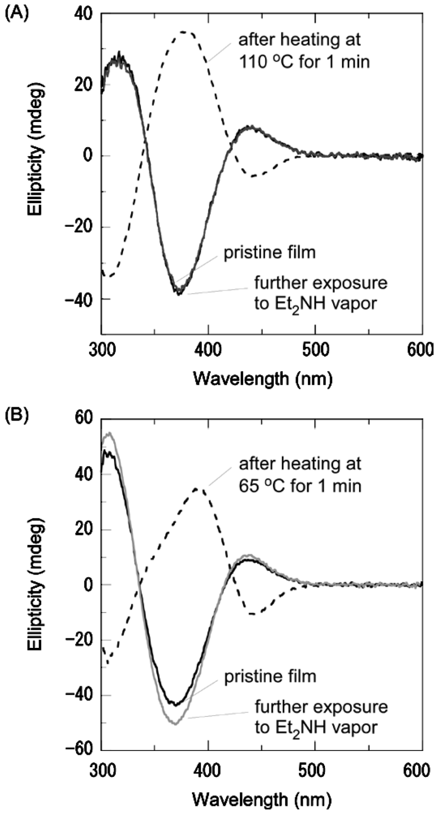

Figure 10. (A) CD spectra of poly(**3**) spin-cast films from 4 wt % Et_2NH solution before (black solid line) and after heating at 110 °C for 1 min (black dashed line) and then further exposure to Et_2NH vapor for 1 min at ordinary temperature and pressure (gray solid line). (B) CD spectra of poly((*S*)-**4**) spin-cast films from 4 wt % Et_2NH solution before (black solid line) and after heating at 65 °C for 1 min (black dashed line) and then further exposure to Et_2NH vapor for 1 min at ordinary temperature and pressure (gray solid line). Spectra were measured at 20 °C.

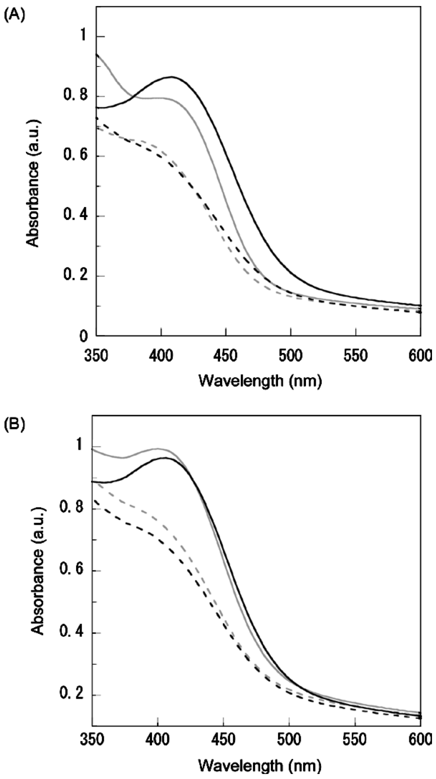

Figure 11. (A) Polarized absorption spectra of poly((*S*)-**4**) draw films on elastic substrate for 1.5 times before (black line) and after (gray line) exposure to acetone vapor for 1 min. (B) Polarized absorption spectra of poly((*S*)-**4**) draw films on elastic substrate before (black line) and after (gray line) heating at 65 °C for 1 min. Angles between polarized and drawing direction are 0° (solid line) and 90° (dashed line).

of polymer main-chain axis should be unchanged during the inversion of main-chain helicity. Therefore, helix−helix transition of the polymer molecules should not proceed via random-coil phase. The rapid inversion even in the solid film is probably due to helix−helix transition. A similar mechanism of helix−helix transition by thermal treatment has been reported for polypeptide film, which was confirmed by using XRD measurement.[14]

Control of Highly Induced CD. In some chiral conjugated polymers, formation of chiral aggregates enlarge the g_{CD} value of the film depending on the kind and the concentration of casting solvent.[12b,c,16c,d,17−20] Poly((*S*)-**4**) film that had been obtained from 4 wt % $CHCl_3$ solution showed a more split CD pattern consisting of a negative first Cotton effect at 475 nm, a positive second one at 433 nm, a positive third one at 365 nm, and a negative fourth one at 322 nm (Figure 12). The absolute value of g_{CD} maximum was 1.90×10^{-2} at 322 nm, which was 1 order larger than that of the film from 4 wt % Et_2NH (1.15×10^{-3} at 370 nm). The mirror image of the highly induced CD spectra of poly((*R*)-**4**) and poly((*S*)-**4**) in the films indicated that these spectra did not depend on both the macroscopic anisotropy[26] and the spin direction of the spin-coater.[27] POM observation revealed that poly((*S*)-**4**) in 20 wt % $CHCl_3$ solution formed cholesteric phase (Figure 13), while no texture was observed in 20 wt % Et_2NH solution. It should be noted that the highly induced CD is obtained in the films from the solvent in which polymers can form liquid crystals.[12d]

Relationship between the highly induced CD spectra and the morphology was examined. The poly(**4**) film from 4 wt % $CHCl_3$ solution showed a XRD peak corresponding to a *d*-spacing of 2.15 nm indicative of a comblike intermolecular aligned structure, while the film from 4 wt % Et_2NH solution was amorphous (Figure 14). Moreover, SEM observation revealed that the poly((*S*)-**4**) film from $CHCl_3$ solution formed helical fibers on an extensive area of the film surface (Figure 15A), while this nanometer-size structure was not observed in the film from Et_2NH solution. Hence, the characteristic morphology and the surface structure of lyotropic liquid crystalline poly(phenylacetylene) were formed only in the film from $CHCl_3$ solution which showed the highly induced CD spectrum. This characteristic surface structure was not also observed in poly(**1**) and poly(**3**) film that did not show the highly induced CD and the lyotropic liquid crystallinity. These results indicate that the highly induced CD spectra are related with the self-assembly formation of a predominantly chiral organization.

The stability of the highly induced CD was examined. In the CD spectrum of the poly((*S*)-**4**) film from 4 wt % $CHCl_3$ solution, only small decrease in the CD intensities at 322 and 433 nm was observed at 100 °C. The CD spectral change was reversible. Hence, the chiral organization was thermally

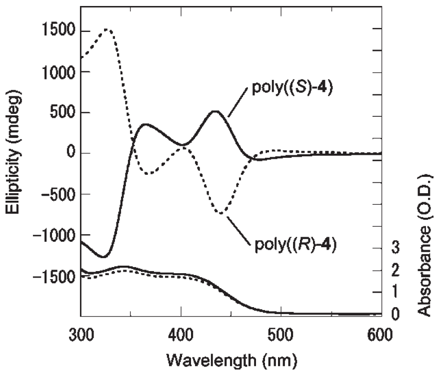

Figure 12. CD (top, left axis) and absorption (bottom, right axis) spectra of poly((*S*)-**4**) (solid line) and poly((*R*)-**4**) (dashed line) spin-cast films from 4 wt % $CHCl_3$ solution.

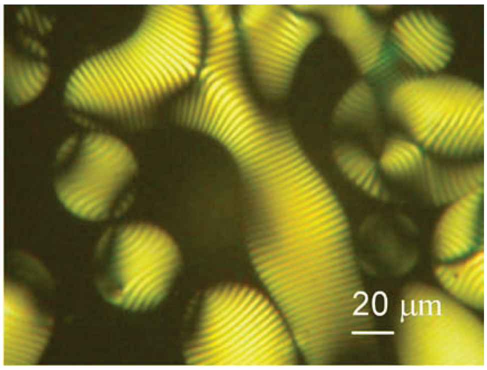

Figure 13. POM image of poly((*S*)-**4**) in 20 wt % $CHCl_3$ solution.

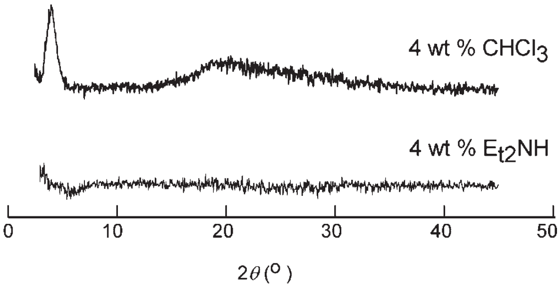

Figure 14. WAXRD patterns of poly((*S*)-**4**) films from 4 wt % $CHCl_3$ and 4 wt % Et_2NH solution.

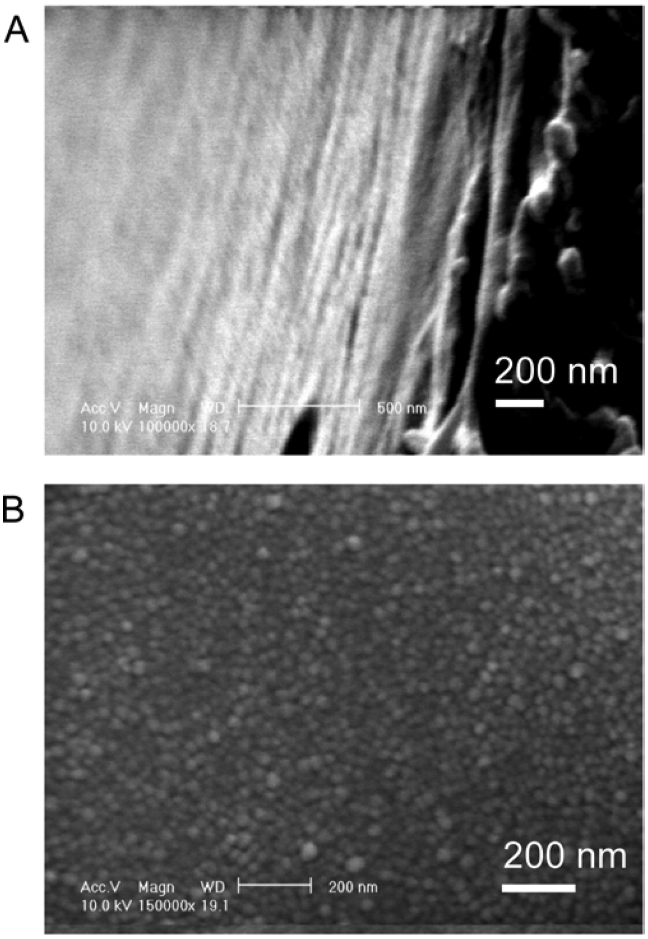

Figure 15. SEM images of poly((*S*)-**4**) film from 4 wt % $CHCl_3$ solution (A) before and (B) after exposure to Et_2NH vapor for 1 min.

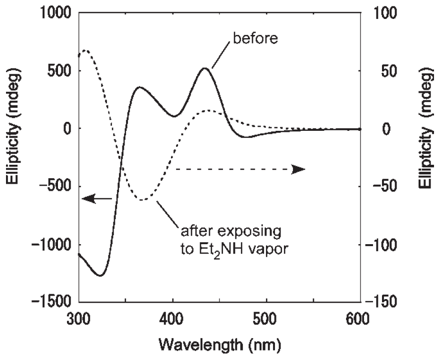

Figure 16. CD spectra of poly((*S*)-**4**) spin-cast film from 4 wt % $CHCl_3$ solution before (solid line, left axis) and after (dashed line, right axis) exposure to Et_2NH vapor for 1 min.

stable below 100 °C. On the other hand, upon exposure to Et_2NH vapor for 1 min, the induced CD spectrum was deformed to change to the similar spectral pattern of the film from Et_2NH (Figure 16). The morphology on the surface of the film after exposure to Et_2NH vapor was also different; i.e., transformation from the helical fiber structure to nanometer-size particle was observed (Figure 15B). There was no deformation of the induced CD by other solvent vapors such as $CHCl_3$, toluene, THF, acetone, and MeOH. Thus, it was revealed that the chiral organization in the film was stable for these external stimuli except for Et_2NH vapor. Regeneration of chiral organization by solvent vapor was attempted, though further exposure to solvent vapors such as $CHCl_3$, toluene, THF, acetone, and MeOH was not effective.

Conclusion

The reversible color change from yellow to orange or red along with the drastic change of helical conformation could be achieved in the poly(*p*-alkoxylphenylacetylene) film by exposure to appropriate solvent vapor and/or by heating. It was revealed that elongation of π-conjugation was mainly induced in the direction of the main-chain axis probably by the intermolecular interaction without *cis*−*trans* isomerization. The reversible and rapid inversion of helical chirality of poly(*p*-alkylphenylacetylene)s in the films could be induced without color change by exposure to appropriate solvent vapor and/or by heating. This rapid inversion is due to the helix−helix transition, not via random-coil phase, because the orientation of the main-chain axis retained. Poly(*p*-alkylphenylacetylene) with a longer alkyl group could inverse the CD at lower temperature. The highly induced CD and helical fibril structures in the film due to the formation of a predominantly chiral organization could be obtained for lyotropic liquid crystalline poly(*p*-alkylphenylacetylene) by selecting the kind of the casting solvent and could be deformed by exposure to appropriate solvent vapor. Chiroptical properties of *cis*-poly(phenylacetylene) films could be variously controlled by selecting the kind of substituent at the para position and external stimuli.

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