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Articles

Synthesis of Poly(*p*-phenylene-vinylene) with Chiral Higher-Order Structure from Simple Monomers by Three-Component Coupling Polymerization

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ABSTRACT: The palladium-catalyzed three-component coupling polymerization of *p*-bromophenylallene and a chiral nucleophile, sodium di-(−)-menthyl methylmalonate, was carried out to give a derivative of poly(*p*-phenylene-vinylene) having chiral substituents on each vinylene unit. For example, a polymer ($M_n = 4800$, $M_w/M_n = 1.6$) was obtained in a high yield by the polymerization in 1,4-dioxane at 80 °C for 24 h in the presence of Pd-$(OAc)_2/4P(o\text{-tolyl})_3$ catalyst. The obtained polymer is soluble in common organic solvents and supposed to have a single-handed helical conformation on the basis of its circular dichroism (CD) spectrum which exhibited a clear Cotton effect within the range of its $\pi-\pi^*$ transition absorption ($\lambda = 250-400$ nm). The nature of the chiral higher-order structure of the polymer was studied in detail by the dependence of the CD spectra of the polymer on the molecular weight and on the character of the solvents.

Introduction

π-Conjugated polymers have been attracting great interest due to their important properties suitable for electronic and optoelectronic applications such as rechargeable batteries and electroluminescent devices.[1] Among them, chiral polymers have began to be paid attention to because of their potential for many advanced applications.[2] For instance, poly(*p*-phenylene-vinylene)s (PPVs),[3a−c] poly(*p*-phenylene-ethynylene)s,[3d−f] polyfluorenes,[3g−i] and polythiophenes[3j] with single-handed helical conformation have been supposed to be applicable to polarized photo- and electroluminescent materials.[3]

The palladium-catalyzed coupling polymerization systems are quite useful strategies for the synthesis of various π-conjugated polymers. For instance, the applications of the Suzuki−Miyaura coupling,[4] the Stille coupling,[5] the Mizorogi−Heck coupling,[6] and the Sonogashira coupling[7] reactions made it possible to prepare a variety of π-conjugated polymers.[8] However, poor processability and solubility of the resulting polymers often require the complicated multistep syntheses of designed monomers. For the preparation of functionalized π-conjugated polymers such as chiral polymers, it is also important to introduce appropriate functionality into monomers for these condensation polymerization processes.

We have been working on the three-component coupling polymerization systems which enable the synthesis of functionalized polymers having well-defined sequence.[9,10] For example, PPV derivatives could be obtained on the basis of the palladium-catalyzed three-component coupling reaction of allene derivatives, aryl halides, and nucleophiles.[11] That is, the palladium-catalyzed three-component coupling polycondensation of 1,4-diallenylbenzene, 1,4-diiodobenzene, and sodium diethyl methylmalonate or that of *p*-bromophenylallene and nucleophiles gives PPVs possessing substituents on each vinylene unit in high yields.[9d,e,i] Compared to the conventional polycondensation methods for PPVs that consist of two monomer components, the three-component system must be advantageous to design functionalized PPVs from simple monomers. Namely, PPVs with unique features will be obtainable by the simple molecular design of the nucleophiles.

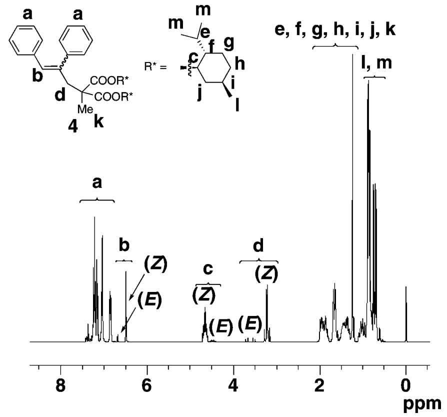

Figure 1. ^{1}H NMR spectrum of **4**.

In this paper, we would like to report the synthesis of a chiral poly(*p*-phenylene-vinylene) by the palladium-catalyzed three-component coupling polymerization of *p*-bromophenylallene and sodium di-(−)-menthyl methylmalonate as a chiral nucleophile. Properties of the resulting chiral PPV are also discussed.

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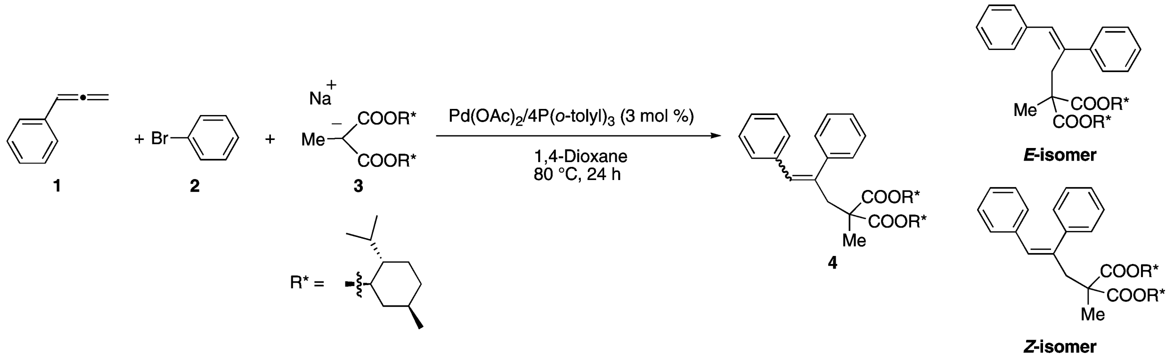
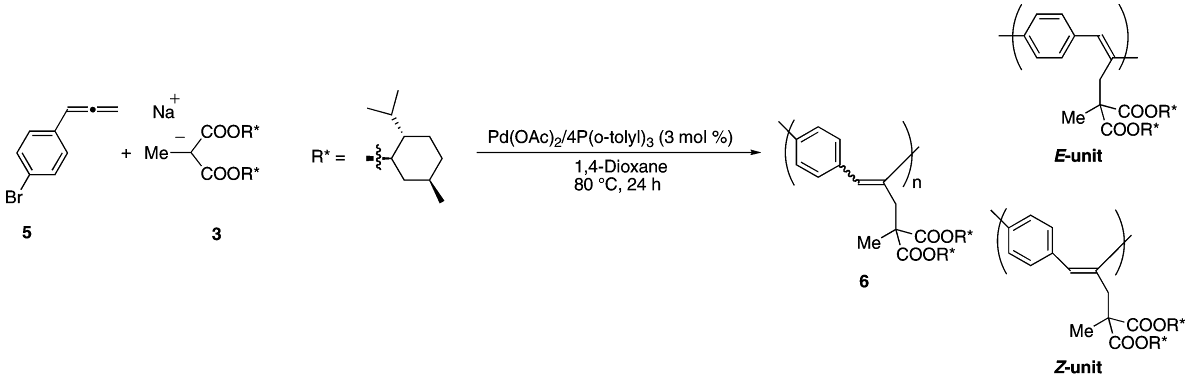
Scheme 1. Three-Component Coupling Reaction of 1, 2, and 3



Scheme 2. Three-Component Coupling Polymerization of 5 and 3



Experimental Section

Instruments. Nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECP-300 instrument (300 and 75 MHz for ^{1}H NMR and ^{13}C NMR, respectively). Fourier transform-infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMH$_{HR}$-M tandem columns using chloroform ($CHCl_3$) as an eluent at 35 °C. Polystyrene standards were used for the calibration. The fractionation of polymer samples was carried out on a JAI LC-908 recycling preparative high performance liquid chromatograph (HPLC) equipped with JAIGEL-2H tandem columns using chloroform ($CHCl_3$) as an eluent. Ultraviolet−visible (UV−vis) spectra were recorded on a Shimadzu UV-3100 spectrometer. Specific rotation was measured in a 10 cm cell at room temperature (approximately 20 °C) in $CHCl_3$ with a JASCO DIP-1000 digital polarimeter. Circular dichroism (CD) spectra were recorded on a JASCO J-805 spectropolarimeter.

Materials. Phenylallene (**1**) and *p*-bromophenylallene (**5**) were prepared by the reported manner.[12] Bromobenzene (**2**) was distilled under nitrogen. Tri-*o*-tolylphosphine was purified by recrystallization from *n*-hexane. 1,4-Dioxane and tetrahydrofuran (THF) were dried over sodium metal and distilled under nitrogen. Other reagents were used as received.

Synthesis of Sodium Di-(−)-menthyl Methylmalonate (3). In a flask equipped with a Dean−Stark apparatus, a mixture of methylmalonic acid (1.65 g, 14.0 mmol), (−)-menthol (4.69 g, 30.0 mmol), *p*-toluenesulfonic acid monohydrate (0.571 g, 3.00 mmol), and benzene (250 mL) was heated under reflux for 24 h. After removal of the volatile fractions under reduced pressure, the purification by column chromatography on SiO_2 (eluent: benzene) gave di-(−)-menthyl methylmalonate in an 89% yield (4.92 g, 12.5 mmol). $[\alpha]_D = -68.4°$ ($c = 0.1$ g/dL, $CHCl_3$). ^{1}H NMR ($CDCl_3$): $\delta = 0.75-2.02$ (39H, $-CH_3$, $-CH_2$-, and $-CH-$), 3.35−3.42 (1H, $-CH(CO_2-)_2$), 4.67−4.76 (2H, $-O-CH-$). ^{13}C NMR ($CDCl_3$): $\delta = 13.6$, 16.1, 16.3, 20.7, 20.8, 22.0, 23.2, 23.4, 25.8, 26.2, 31.3, 34.2, 40.6, 40.7, 46.6, 46.9, 47.0, 75.1, 169.7, 169.9. IR (neat, cm^{-1}): 2955, 2870, 1748, 1456, 1371, 1318, 1244, 1219, 1167, 1150, 1096, 1034, 1009, 982, 963, 910, 893, 876, 845.

The treatment of this ester with NaH provides the nucleophile (**3**) as follows: to a flask equipped with a dropping funnel and a magnetic stirrer bar, was added NaH (55 wt % in oil, 0.305 g, 7.00 mmol) and was washed three times with *n*-hexane. After the removal of the remaining solvent under reduced pressure, THF (20 mL) was introduced to the flask and a THF (20 mL) solution of di-(−)-menthyl methylmalonate (2.76 g, 7.00 mmol) was added slowly from the dropping funnel and the resulting mixture was kept stirring for an additional 5 h at room temperature. After filtration and evaporation of the volatile fractions under reduced pressure, the white solid remaining was washed several times with *n*-hexane and was dried under vacuum. The obtained nucleophile (**3**) was dissolved in 1,4-dioxane, and the 1,4-dioxane solution (1.0 M) was used for the model reactions and the polymerizations.

Model Reaction. Coupling Reaction of Phenylallene (1), Bromobenzene (2), and Sodium Di-(−)-menthyl Methylmalonate (3). To a test tube equipped with a magnetic stirrer bar, a 1,4-dioxane solution of **3** (1.0 M, 2.0 mL, 2.0 mmol) was introduced and the solvent was removed in vacuo. Then, tri-*o*-tolylphosphine (0.036 g, 0.12 mmol), palladium acetate ($Pd(OAc)_2$, 0.0068 g, 0.030 mmol), and 1,4-dioxane (2.0 mL) were added, and the mixture was kept stirring at room temperature for 10 min under nitrogen. After the addition of **1** (0.116 g, 1.0 mmol) and **2** (0.157 g, 1.0 mmol), the mixture was stirred at 80 °C for 24 h. After pouring the resulting mixture into water (5 mL), the organic layer was collected, and the aqueous phase was extracted with three 2 mL portions of diethyl ether. The organic layer was dried over magnesium sulfate. After filtration and removal of the solvent, the residue was purified by SiO_2 column chromatography (eluent of *n*-hexane/ethyl acetate, v/v = 10/1) to give chiral stilbene derivatives (**4**) in a 71% yield (0.42 g, 0.71 mmol) as a mixture of *E*- and *Z*-isomers. $[\alpha]_D = -33.5°$ ($c = 0.1$ g/dL, $CHCl_3$). ^{1}H NMR ($CDCl_3$): $\delta = 0.59-1.98$ (39H, $-CH_3$, $-CH_2-$, and $-CH-$), 3.16−3.28 (2H × 0.90, $-C{=}C-CH_2-$, *Z*), 3.50−3.72 (2H × 0.10, $-C{=}C-CH_2-$, *E*), 4.41−4.54 (2H × 0.10, $-O-CH-$, *E*), 4.55−4.71 (2H × 0.90, $-O-CH-$, *Z*), 6.49 (1H × 0.90, $-C-C{=}CH-$, *Z*), 6.69 (1H × 0.10, $-C-C{=}CH-$, *E*), 6.84−7.43 (10H, $-C_6H_5$). ^{13}C NMR ($CDCl_3$): $\delta =$ 15.9, 16.2, 20.1, 20.9, 22.0, 23.1, 25.8, 31.3, 34.2, 40.4, 40.6, 44.5, 46.9, 55.1, 75.3, 75.4, 126.3, 127.1, 127.7, 128.3, 128.4, 129.1, 130.9, 137.0, 138.0, 141.2, 171.5, 171.7. IR (neat, cm^{-1}): 3056, 3023, 2957, 2870, 1725, 1493, 1456, 1372, 1289, 1244, 1111, 1038, 982, 916, 874, 754. From the ^1H NMR spectrum of **4**, the ratio of *E*- and *Z*-isomers in **4** was determined to be 10:90.

Polymerization. Coupling Polymerization of *p*-Bromophenylallene (5) and Sodium Di-(−)-menthyl Methylmalonate (3). To a test tube equipped with a magnetic stirrer bar, a 1,4-dioxane solution of **3** (1.0 M, 1.0 mL, 1.0 mmol) was introduced and the solvent was removed in vacuo. Then, tri-*o*-tolylphosphine (0.018 g, 0.060 mmol), palladium acetate ($Pd(OAc)_2$, 0.0034 g, 0.015 mmol), and 1,4-dioxane (2.0 mL) were added, and the mixture was kept stirring at room temperature for 10 min under nitrogen. After the addition of **5** (0.098 g 0.50 mmol), the mixture was stirred at 80 °C for 24 h. The resulting mixture was poured into water (5 mL), the organic layer was collected, and the aqueous phase was extracted with three 2 mL portions of chloroform. After drying over magnesium sulfate, the organic layer was evaporated under vacuum. Then, the residue was dissolved in $CHCl_3$ (2 mL) and was precipitated into a large excess amount of methanol to give a polymer (**6**) in an 84% yield (0.20 g, 0.42 mmol unit). $[\alpha]_D = -62.9°$ ($c = 0.1$ g/dL, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta = 0.50-2.17$ (39H, $-CH_3$, $-CH_2-$, and $-CH-$), 2.88−3.33 (2H × 0.76, $-C{=}C-CH_2-$, *Z*), 3.33−3.83 (2H × 0.24, $-C{=}C-CH_2-$, *E*), 4.36−4.89 (2H, $-O-CH-$), 6.22−7.44 (5H, $-C-C{=}CH-$ and $-C_6H_4-$). ^{13}C NMR ($CDCl_3$): $\delta = 15.9$, 16.2, 20.1, 20.9, 22.0, 23.1, 25.8, 31.3, 34.2, 40.5, 40.7, 44.6, 46.9, 55.3, 75.3, 128.4, 129.1, 130.1, 130.7, 135.8, 137.5, 139.6, 171.4, 171.6. IR (neat, cm^{-1}): 2955, 2870, 1724, 1508, 1458, 1371, 1290, 1244, 1111, 1038, 1009, 982, 912, 845, 756. From the ^1H NMR spectrum of **6**, the ratio of *E*- and *Z*-units in **6** was determined as 24:76.

Likewise, the polymerization of **5** and sodium di-(+)-menthyl methylmalonate gave a polymer (**(+)-6**) in an 82% yield ($M_n = 4400$, $M_w/M_n = 1.4$). $[\alpha]_D = +61.9°$ ($c = 0.1$ g/dL, $CHCl_3$).

Results and Discussion

Model Reaction. In accordance with the previous report on the palladium-catalyzed ternary coupling reaction of phenylallene (**1**), iodobenzene, and sodium diethyl methylmalonate, which gives three-component coupling products in a 79% yield, stilbene derivatives (**4**) were obtained in a 71% yield by the reaction of **1**, bromobenzene (**2**), and sodium di-(−)-menthyl methylmalonate (**3**) in 1,4-dioxane at 80 °C for 24 h in the presence of $Pd(OAc)_2/4P(o\text{-tolyl})_3$ (3 mol %) (Scheme 1). From the ^1H NMR spectrum of **4**, peaks for the olefinic protons in the *E*- and *Z*-isomers were observed at 6.69 and 6.49 ppm, respectively. Peaks for the allylic protons in the *E*- and *Z*-isomers were also observable at 3.16−3.28 and 3.50−3.72 ppm, respectively (Figure 1).[13] On the basis of the integral ratio of these peaks, the ratio of *E*/*Z* in **4** was determined to be 10:90. Compared to the case of sodium diethyl methylmalonate giving the *E*-rich products (*E*/*Z* = 60:40), the higher *Z*-isomer-content in **4** is most probably due to the steric bulkiness of the nucleophile (**3**).[14]

Polymerization. The polymerization of *p*-bromophenylallene (**5**) and **3** was carried out in 1,4-dioxane at 80 °C for 24 h in the presence of $Pd(OAc)_2/4P(o\text{-tolyl})_3$ (3 mol %) (Scheme 2). As a result, a PPV derivative having di-(−)-menthyl ester moieties in each vinylene unit (**6**, $M_n = 4800$, $M_w/M_n = 1.6$) was obtained in an 84% yield as a yellow powdery solid. Compared to the poor solubility of the unsubstituted PPV ($(-C_6H_4-CH{=}CH-)_n$) prepared by the Heck coupling reaction of *p*-bromostyrene,[15] **6** exhibits remarkably high solubility in common organic solvents such as THF, $CHCl_3$, and benzene, most probably due to the di-(−)-menthyl methylmalonate moieties on the vinylene units.

The proposed structure of the obtained polymer (**6**) was fully supported by its ^1H NMR, ^{13}C NMR, and IR spectra. The ^1H NMR spectrum of **6** also gave information on the ratio of *E*- and *Z*-units in **6** to be 24:76 (Figure 2). As we described previously,[9e] the polymer obtained from **5** and sodium diethyl methylmalonate has the predominant *E*-unit (*E*/*Z* = 68:32). The higher *Z*-unit content in **6** is consistent with the model reaction and is also ascribable to the steric bulkiness of the nucleophile (**3**), as mentioned above.

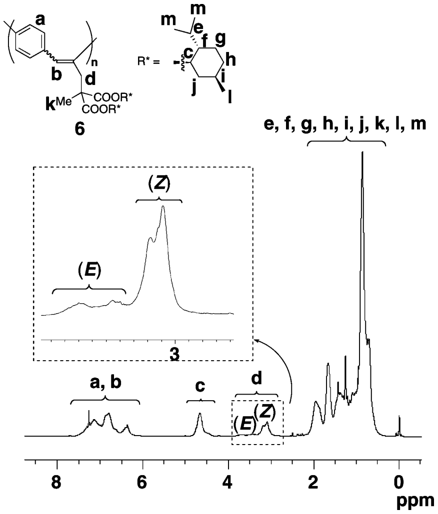


Figure 2. ^1H NMR spectrum of **6**.

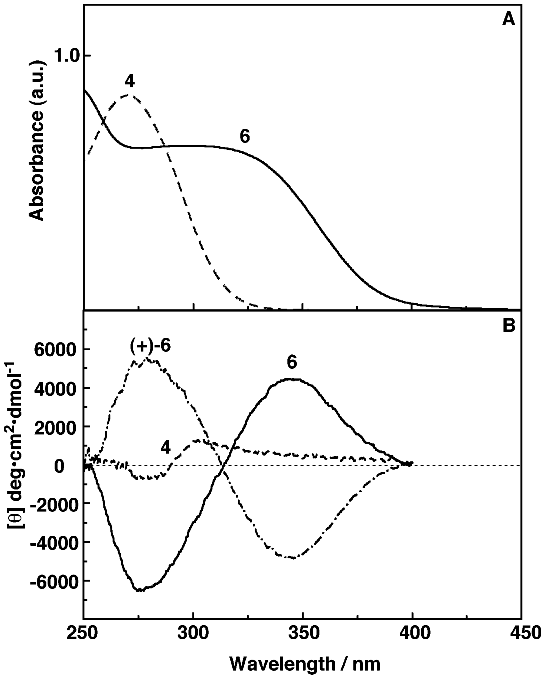


Figure 3. UV−vis absorption spectra of **4** and **6** in $CHCl_3$ (1.0×10^{-5} M) (A). CD spectra of **4**, **6**, and **(+)-6** in $CHCl_3$ (B).

Optical Properties. In the UV−vis spectrum of the polymer (**6**), the absorption maximum (λ_{max}) was observed at 305 nm in a $CHCl_3$ solution, which is bathochromically shifted by 35 nm in comparison with that of the model compounds (**4**) (Figure 3A). The λ_{max} of **6** was obviously blue-shifted in comparison with that of the reported unsubstituted poly(*p*-phenylenevinylene) ($\lambda_{max} = 420$ nm),[16] most probably due to the distortion of the main chain planarity caused by the repulsion of the substituents attached to the vinylene units. In the photoluminescence spectrum, **6** exhibited blue light with an emission maximum of 458 nm upon the irradiation at 305 nm, while no emission was observed in the case of the model compounds (**4**) (Figure 4).

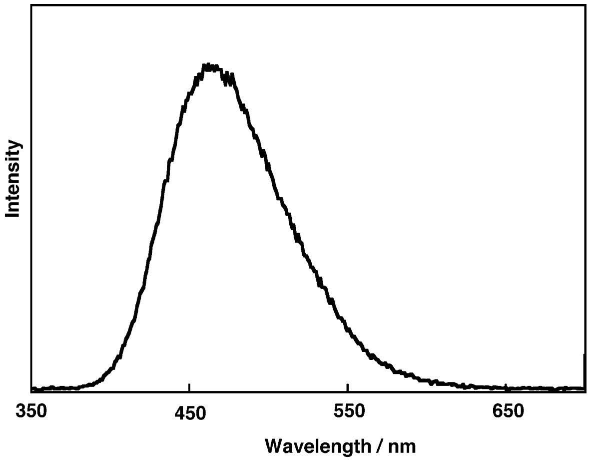


Figure 4. Photoluminescence spectrum of **6** in $CHCl_3$.

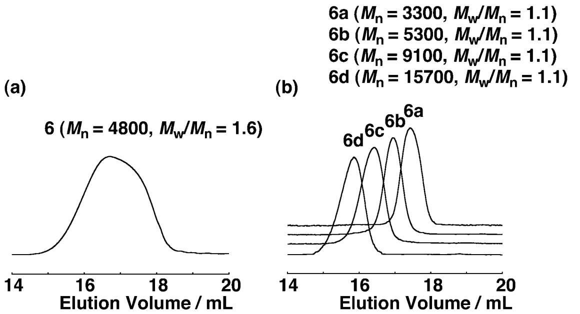


Figure 5. GPC profiles of **6** (a) and its fractions separated by preparative HPLC (**6a**−**d**) (b).

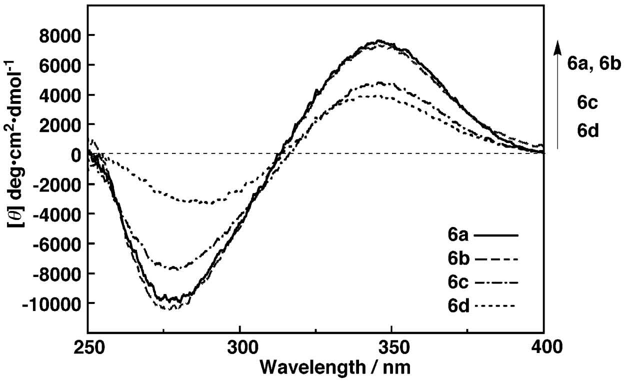


Figure 6. CD spectra of **6a**−**d** in $CHCl_3$.

The circular dichroism (CD) spectra of **6** in a $CHCl_3$ solution exhibited a clear Cotton effect in the range of its $\pi-\pi^*$ transition (λ = 250−400 nm), while the corresponding effect was not observable in that of **4**. These results can be taken to mean that **6** has the chiral higher-order structure in $CHCl_3$. The CD spectrum of the polymer (**(+)-6**) from di-(+)-menthyl methylmalonate appeared as a mirror image to that of **6** which was consistent with the idea that the polymer has an enantiomeric chiral higher-order structure. (Figure 3B).

The polymer (**6**) was divided into four fractions (M_n = 3300, 5300, 9100, and 15 700) by HPLC to evaluate the relationship between the chiral higher-order structure and the molecular weight of **6** (Figure 5).[17] In the CD spectra of these fractions (Figure 6), the intensity of the signals gradually increased until M_n of **6** increased to 9100 and become constant at a much higher M_n region. The result may indicate that the chiral higher-order structure of **6** is stabilized by the elongation of the chain length.

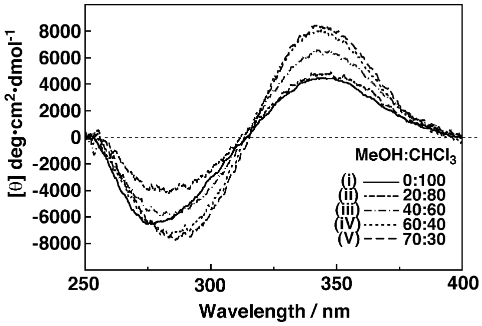


Figure 7. CD spectra of **6** in MeOH/$CHCl_3$ mixed solvents (v/v = 0/100 (i), 20/80 (ii), 40/60 (iii), 60/40 (iv), and 70/30 (v)).

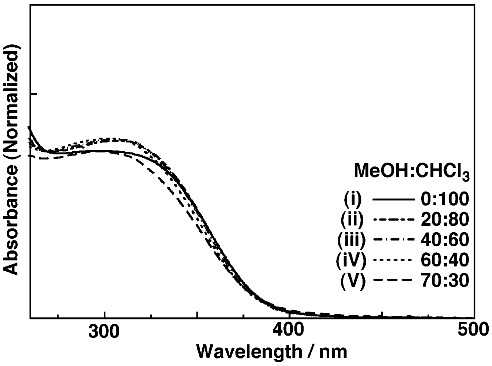


Figure 8. UV−vis spectra of **6** in MeOH/$CHCl_3$ mixed solvents (v/v = 0/100 (i), 20/80 (ii), 40/60 (iii), 60/40 (iv), and 70/30 (v)).

The chiroptical property of the polymer (**6**) was evaluated in mixed solvents consisting of poor and good solvents such as MeOH/$CHCl_3$. As shown in Figure 7, the intensity of CD signals increased slightly by increasing the methanol content in MeOH/$CHCl_3$ from 0% to 70%. Under these conditions, **6** dissolved completely in the mixed solvents, while the polymer started to precipitate if the MeOH content increased further (>70%). In the cases of some of the chiral π-conjugated polymers such as poly(*p*-phenylene-vinylene),[18a] poly(*p*-phenylene-ethynylene),[18b−d] polythiophene,[18e−g] and poly(thienylene-vinylene)[18h−j] in which the chiral superstructures were induced by means of the intermolecular $\pi-\pi$ stacking process, the nature of the solvents largely affects the higher ordered structures. Compared to these systems, the difference observed in the CD spectra of **6** was substantially small.[19] It is also of note that the UV−vis absorption spectra of **6** were almost independent of the solvents (Figure 8), while noticeable changes have been reported for the polymers providing intermolecular $\pi-\pi$ stacking−induced chiral superstructures.[20] Accordingly, the chiral higher-order structure of **6** is most probably induced along the backbone of each polymer chain.

Conclusions

A derivative of chiral poly(*p*-phenylene-vinylene) possessing chiral substituents on each vinylene unit was obtained in a high yield by the palladium-catalyzed three-component coupling polymerization of *p*-bromophenylallene and a chiral nucleophile, sodium di-(−)-menthyl methylmalonate. The CD spectra of the obtained polymer exhibited a clear Cotton effect within the range of its $\pi-\pi^*$ transition absorption, and the spectra were not influenced largely by the nature of the solvents, suggesting that the each polymer chain has the induced chiral higher-order structure along the backbone due to the chiral substituent on each vinylene unit.

On the basis of the current polymerization technique, a variety of chiral poly(*p*-phenylene-vinylene)s are expected to be designed simply by varying chiral nucleophiles. Thus, the synthesis and properties of the series of chiral polymers are currently being investigated.

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(20) In the case of the polymer reported in ref. 18b, $\lambda_{\max}$ of the UV−vis absorption spectra exhibited a clear bathochromic shift of 30−40 nm by using mixed solvents containing poor solvents due to the formation of the intermolecular $\pi-\pi$ stacking chiral superstructure.

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