Polycondensation for Synthesis of Multi-functional Products

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Abstract. Miyaura-Suzuki type polycondensation with no use of n-BuLi for preparation of precursors was carried out to obtain a series of π-conjugated materials having multi-functionality. Bulky substituent in the monomer restricts propagation in the polycondensation to give high molecular weight products. Although the products thus obtained show low molecular weight, the resultant materials show good optical absorption and fluorescence.

Introduction

π-Conjugated polymers have attracted much attention among numerous scientists and engineers because of their applications for organic light emitting diodes (OLEDs) [1], photovoltaic cells (PVCs) [2], biological sensors [3, 4], organic thin film transistors (OTFTs) [5] and bio-electrochromic devices [6]. Therefore, much interest has been concentrated on developing novel properties of conjugated polymers. The synthesis of conjugated polymers with high quality is often a challenge for chemists. Palladium-catalyzed Suzuki coupling reaction [7–9] is one of the most important methods.

The palladium-catalyzed Suzuki-Miyaura coupling of organoborons with aryl halides is known as one of the most useful carbon-carbon bond-forming reactions [10-18]. It is a versatile and selective method for formation of aryl–aryl bonds. Besides, it also has advantages to allow introduction of a wide range functional side chains in the polymer. Furthermore, this method involves low toxicities of the precursors and easy handling even under air and tolerating a large number of functional groups [19-21]. Different types of functional groups endow conjugated polymers with different properties and applications. Gong et al. report the synthesis of cationic polymers with Suzuki coupling method and made light-emitting diodes. The devices with electron-transport layer have significantly lower turn-on voltages, higher brightness [22].

In this work, we synthesized a series of π-conjugated materials with Miyaura-Suzuki coupling reaction for exploration of new type coupling and new functional products. We employed phenylene, thiophene and fluorene rings as main chains (Scheme 1). Flexible alkyl group, azobenzene, and optically active groups was introduced into conjugated polymer as side chains. Especially, introduction of chiral group allow to obtain chiral conjugated polymers due to formation of chiral higher order structures [23,24]. Optical and electronic properties of the polymers synthesized in this study were examined with UV-vis absorption, photoluminescence, and circular dichroism spectroscopies. The CD of P1 shows negative Cotton effect at 331 nm and a positive at 274 nm, which corresponds to an optical absorption band at around 280 nm, indicating the polymer form one-handed chiral structure. The resultant products showed low-molecular weight. This may be due to the fact that steric hindrance between substituents of monomer blocks depresses progress of the polymerization, indicating Miyaura-Suzuki type polycondensation need to consider steric...
hindrance to obtain polymers. However, this reaction can afford to yield polymers having multi-functionality, such as light isomerization and chiroptical activity (Scheme 2). In general, n-BuLi with high activity needs to be used in the preparation of precursor of monomers for Miyaura-Suzuki coupling. This reaction has limitation for reactions to produce functional polymers because n-BuLi reacts with ester group and amino groups, yielding a desired product (Scheme 3(1)). While, diborane compound to prepare the precursor allows no use of n-BuLi for preparation of precursor (Scheme 3(2)), expanding possibility of the Miyaura-Suzuki polycondensation reaction.

In this report, the resultant product was referred to as polymeric materials conveniently, although this polycondensation produces low-molecular materials at the present stage.

Scheme 1. Synthesis of monomers and polycondensation.

Scheme 2. Advantage and disadvantage of the reaction in this study.
Scheme 3. Synthesis of a precursor compound for Miyaura-Suzuki type polycondensation.

Chemicals

Commercially available reagents were received from Nacalai Tesque (Japan), Sigma-Aldrich (Japan), Kanto Chemical (Japan) and Tokyo Chemical Industry (Japan) and used without further purification. Common organic solvents such as dichloromethane and tetrahydrofuran (THF) were distilled and handled in a moisture-free atmosphere. The purification of the newly synthesized compounds was performed by column chromatography on silica gel (Silica gel 60 N).

Techniques.

$^1$H NMR spectra of the compounds were recorded using JNM ECS 400 spectrometer (JEOL, Japan) with CDCl$_3$ as the deuterated solvent and tetramethylsilane (TMS) as the internal standard. The chemical structure and optical properties of a series of polymers were confirmed with infrared (IR) spectroscopy (Jasco, Japan, FT-IR 500 spectrometer using the KBr method) and UV-vis spectroscopy (Jasco, Japan, V-630 spectrophotometer). Circular dichroism (CD) absorption spectra were obtained with a J-720 spectrometer (Jasco, Japan). Differential scanning calorimetry (DSC) analysis was conducted with Exstar 7000 (SEIKO Instruments, Japan). Photoluminescence (PL) spectra of the polymers in chloroform were measured with F-4500 fluorescence spectrophotometer (HITACHI, Japan). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analysis was conducted using TOF/TOF 5800 (AB SCIEX, USA) with dithranol as a matrix. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) against polystyrene standards by using THF as a solvent with 5 μm MIXED-D column (Polymer Laboratories), PU-980 HPLC pump (Jasco, Japan), and MD-915 multi-wavelength detector (Jasco, Japan).

Synthesis

Butyl 2,5-dibromobenzoate (1).

2,5-Dibromobenzoic acid (1.00 g, 3.50 mmol), 1-butanol (1.20 g, 14.3 mmol), and 4-dimethylaminopyridine (DMAP, 0.109 g, 0.89 mmol) were dissolved in 50 mL of dry...
dichloromethane in a 250mL a two-necked round-bottom flask filled with nitrogen. The solution was cooled to 0 – 5 °C with an ice-water bath, to which N,N'-dicyclohexylcarbodiimide (DCC, 2.40 g, 11.8 mmol) in 50 mL of dichloromethane was added under stirring via a dropping funnel. The reaction mixture was stirred overnight. After filtering out the formed insoluble urea, the filtrate was concentrated by a rotary evaporator. The product was purified by a silica gel column using ethyl acetate/hexane (v/v = 1:20) as the eluent. The product is colorless oil. Yield: 84.5%. \(^1\)H NMR (400MHz, CDCl\(_3\), \(\delta\), ppm): 8.32 (s, 1H, Ar–H), 7.93–7.92 (d, 1H, J = 8, Ar–H), 7.48–7.46 (d, 1H, J = 8, Ar–H), 4.34–4.30 (t, 2H, J = 10.3, -O-CH\(_2\)(CH\(_2\)Cl)CH\(_3\)), 1.81–1.72 (m, 2H, -OCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.63–1.51 (m, 2H, -OCH\(_2\)CH\(_2\)-CH\(_2\)CH\(_3\)), 0.99–0.97 (t, J = 11.2, 3H, -OCH\(_2\)(CH\(_2\))=CH\(_3\)).

**Butyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2).**

Butyl 2,5-dibromobenzoate (1.00 g, 2.87 mmol), [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) complex with dichloromethane (PdCl\(_2\)(dppf)CH\(_2\)Cl\(_2\), 0.0814 g, 0.10 mmol), potassium acetate, (KAcO\(_2\), 1.69 g, 17.2 mmol) and bis(4,4,5,5-tetramethyl-[1,3]dioxolan-2-yl) borane (1.02 g, 4.31 mmol) were added into a three necked round bottom with 1,4-dioxane 20 mL under an argon stream. The mixture was heated to 90 °C with stirring for ca. 16h. After cool to room temperature, the reaction mixture was extracted with CH\(_2\)Cl\(_2\) three times. The organic layer was washed with water and dried over with anhydrous MgSO\(_4\). After evaporation of the solvents, the product was purified by a silica gel column using ethyl acetate/hexane (v/v = 1:20) as an eluent. The product is yellow solid. Yield: 65.3%. \(^1\)H NMR (400MHz, CDCl\(_3\), \(\delta\), ppm): 8.31 (s, 1H, Ar–H), 7.92–7.90 (d, 1H, J = 8, Ar–H), 7.49–7.47 (d, 1H, J = 8, Ar–H), 4.34–4.30 (t, 2H, J = 10.3 -O-CH\(_2\)(CH\(_2\)CH\(_2\)CH\(_3\)), 1.81–1.72 (m, 2H, -OCH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\)), 1.63–1.51 (m, 2H, -OCH\(_2\)CH\(_2\)-CH\(_2\)CH\(_3\)), 1.41–1.33 (m, 24H, -CC-(CH\(_3\))\(_2\)), 0.99–0.94 (t, 3H, J = 14.2 , -OCH\(_2\)(CH\(_2\))=CH\(_3\)). m/z = 431.

**P1.** Into a 10 mL three-necked, round-bottom flask containing compound M1 (100 mg, 0.188 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\(_3\))\(_4\)) (10.8 mg, 0.0093 mmol), potassium carbonate (K\(_2\)CO\(_3\), 77.8 mg, 0.564 mmol), monomer 2 (121 mg, 0.282 mmol), and 0.2 mL of water and 2 mL of THF were added under an argon stream. The mixture was heated to 80 °C with stirring for about 68 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was extracted with CH\(_2\)Cl\(_2\). The organic layer was washed with water and dried with over anhydrous MgSO\(_4\). After the evaporation of the solvents, the crude product was diluted in 3 mL of chloroform. The solution was added dropwise to 100 mL of methanol with stirring. The precipitate was allowed to stand overnight and centrifugal separation to obtain 10 mg black solid. Y = 4.59%. \(^1\)H NMR (400MHz, CDCl\(_3\), \(\delta\), ppm): 8.26-6.87 (m, 5H), 4.38-4.04 (m, 4H), 1.82-1.07 (m, 34H), 0.91-0.77 (m, 9H).

**P2.** P2 was synthesized using the same method as synthesis of P1, compound M2 (100 mg, 0.265 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\(_3\))\(_4\)) (15.3 mg, 0.0133 mmol), K\(_2\)CO\(_3\) (109 mg, 0.795 mmol), monomer 2 (171 mg, 0.398 mmol), and 0.2 mL of water and 2 mL of THF. The final product, a brown solid polymer, was obtained after drying in vacuo, with a yield of 6.81%. \(^1\)H NMR (400MHz, CDCl\(_3\), \(\delta\), ppm): 8.38-7.32 (m, 6H), 4.22-4.03 (m, 3H), 1.92-1.06 (m, 17H), 0.93-0.76 (m, 6H).

**P3.** P3 was synthesized using the same method as synthesis of P1, compound M3 (100 mg, 0.232 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh\(_3\))\(_4\)) (13.4 mg, 0.0116 mmol), K\(_2\)CO\(_3\) (96
mg, 0.696 mmol), monomer 2 (149 mg, 0.348 mmol), and 0.2 mL of water and 2 mL of THF. The final product, a brown solid polymer, was obtained after drying in vacuo, with a yield of 4.16%.

P4. P4 was synthesized using the same method as synthesis of P1, compound M4 (100 mg, 0.319 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (19.5 mg, 0.0159 mmol), K₂CO₃ (132 mg, 0.958 mmol), monomer 2 (206 mg, 0.479 mmol), and 0.2 mL of water and 2 mL of THF. The final product, a brown solid polymer, was obtained after drying in vacuo, with a yield of 25.32%. ¹H NMR (400MHz, CDCl₃, δ, ppm): 8.42-7.30 (m, 6H), 4.25-4.04 (m, 3H), 1.94-1.08 (m, 14H), 0.94-0.78 (m, 6H).

P5. P5 was synthesized using the same method as synthesis of P1, compound M5 (100 mg, 0.214 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (12.4 mg, 0.0107 mmol), K₂CO₃ (188 mg, 0.643 mmol), monomer 2 (138 mg, 0.322 mmol), and 0.2 mL of water and 2 mL of THF. The final product, a brown solid polymer, was obtained after drying in vacuo, with a yield of 8.31%. ¹H NMR (400MHz, CDCl₃, δ, ppm): 8.38-7.01 (m, 4H), 4.33-4.05 (m, 4H), 1.92-1.02 (m, 7H), 0.94-0.78 (t, 3H).

P6. P6 was synthesized using the same method as synthesis of P1, compound M6 (25 mg, 0.0508 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (2.9 mg, 0.0025 mmol), K₂CO₃ (21 mg, 0.152 mmol), monomer 2 (32.8 mg, 0.0762 mmol), and 0.2 mL of water and 2 mL of THF. The final product, a brown solid polymer, was obtained after drying in vacuo, with a yield of 5.61%. ¹H NMR (400MHz, CDCl₃, δ, ppm): 8.32-6.96 (m, 13H), 4.42-4.01 (d, 2H), 1.96-1.06 (m, 4H), 1.05-0.78 (t, 3H).

Results and Discussion.

Polycondensation results of P1-P6 are summarized in Table 1. Number average molecular weights (Mₙ) of the conjugated polymers evaluated with gel permeation chromatography (GPC) are corresponding to the result of MALDI-TOF-MS. However, degree of polymerization (DP) is small for polymers P1-P6. This may be due to steric hindrance between the monomers in the reaction process.

| Polymer | Mₙ [g/mol] | Mₖ [g/mol] | Mₖ/Mₙ | DP² | MS³ |
|---------|------------|------------|--------|-----|-----|
| P1      | 2,300      | 5300       | 2.3    | 4   | 2,592|
| P2      | 2,400      | 3,600      | 1.5    | 4   | 2,447|
| P3      | 2,400      | 3,200      | 1.3    | 6   | 2,383|
| P4      | 1,500      | 2,200      | 1.5    | 5   | 1,206|
| P5      | 2,500      | 3,100      | 1.2    | 5   | 2,632|
| P6      | 2,200      | 2,700      | 1.2    | 4   | 2,769|

¹Estimated with GPC using THF as an eluent against polystyrene standard. ²Degree of polymerization (calculated by Mₖ/Mₙ, M: molecular weight of monomer repeat unit). ³MALDI-TOF-MS measurements results of these polymers
Characterization

The products were characterized with the IR spectroscopy. All the polymers gave satisfactory analysis data corresponding to their expected molecular structures. IR spectrums of P1-P6 are shown in Figure 1. All polymers show relatively intense absorptions at 2851 cm\(^{-1}\)-2982 cm\(^{-1}\) due to C–H stretching of the long alkyl chain and C=O stretching band at 1711 cm\(^{-1}\) due to ester groups in the side chain. The polymers also show an absorption band at 1248 cm\(^{-1}\) due to CO-O-C (ester) stretching in the benzoate units. P1 displays relatively intense absorption band at around 1089 cm\(^{-1}\) because of the C–O–C stretching of the M1 units. On the other hand, Ar-H and C-H out-of-plane vibration was observed at 830 cm\(^{-1}\) and 1476 cm\(^{-1}\). Particularly, P1 has an intense absorption band at 830 cm\(^{-1}\) due to \(\pi\)-substituents in benzene ring. These results indicate that the polymerization of aryl halides and butyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate was achieved.

![Figure 1. IR spectra of P1, P2, P3, P4, P5, and P6.](image-url)
Figure 2. $^1$H NMR spectra of butyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate and P6 with deuterated chloroform as solvent. Horizontal axis: $\delta$ from tetramethylsilane (TMS) (ppm).

The structures were verified with the $^1$H NMR spectroscopy. All the peaks of P1-P6 can be readily assigned to the resonances of appropriate protons. The $^1$H NMR spectrum of P6 was shown in Figure 2, as an example. The signals at 0.78–2.07 ppm are attributed to the protons in alkyl chains. The chemical shift at 4.09 ppm in the NMR spectra (Figure 2b) of the benzoate unit (signal ‘d’) was attributable to the chemical shift of the proton in COOCH group. Particularly, the protons of the arylene rings of P6 were observed at around low magnetic field. The aromatic rings of the phenyl groups show signals in the same region as those of the aromatic rings of the fluorene groups.

Optical Properties of Polymers

Figure 3 and Figure 4 show CD spectrum of P1 in THF solution, and optical absorption spectra of P1-P6 in THF solution. P1 shows a clear couplet with a negative CD signal at 331 nm and a positive CD signal at 274 nm, corresponding to an intense optical absorption band at around 280 nm, indicating the formation of helices. However, other polymers did not exhibit the CD signal. The polymers of poly(benzophenylene) type (P1, P2, and P3) have a maximum absorption at 280 nm and 311 nm. The polymers of polybenzothiophene type (P4, P5) show intense absorptions at 338 and 319 nm. An intense absorption of polybenzofluorene type P6 was observed at 347 nm.
Figure 3. Circular dichroism (CD) absorption spectra of P1 in THF solution.

Figure 4. UV-vis absorption spectra of the polymers in THF solution.

Figure 5. Photoluminescence spectra of THF solutions of P1, P2, P3, P4, P5, and P6.

Figure 5 shows fluorescent spectra of the polymers in THF solution. Photoexcitation at 280 nm for poly(benzophenylene) type polymers (P1, P2, and P3) allows intense emission at 421 nm, 412 nm, and 395 nm respectively. Polybenzo thiophene type polymers (P4, P5) show emission peaks at 471 nm, and 443 nm. P6 shows emission at long wavelengths (408 nm). Predominantly, intra-molecular energy transition along the main chain occurs in low concentration of the polymer solution [25].
We carried out a series of polycondensations to obtain six products having benzoate units and aromatic units through Suzuki-Miyaura type polycondensation with an aid of Pd(0) catalyst. All products show optical absorptions at long wavelengths. The chemical structures were characterized; demonstrating well-defined conjugated materials have been prepared. The exploration experiment in this study indicates that the Suzuki-Miyaura coupling polymerization can produce $\pi$-conjugated skeleton, and this reaction allows producing multi-functional chemical materials. However, this polycondensation may not be very effective for compounds having steric hindrance in polycondensation to yield polymer with high molecular weight. Employment of large amount of Pd(0) catalyst, reaction at high temperature ($<140^\circ$C to avoid deactivation of Pd(0)), and irradiation of microwave to increase reaction activity are possibly valid to obtain high molecular weight products.

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