Flow Electrolysisisis and Molecular Weight Control of Polyphenylene Deriving from 1,4-Bis(trimethylsilyl)benzene: Effect of a Silyl Substituent on the Coupling Position

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ABSTRACT

In this study, we have demonstrated electrochemical synthesis of polyphenylene (PP) deriving from 1,4-bis(trimethylsilyl)benzene using a flow microreactor. The electrochemical flow microreactor allowed effective synthesis of a soluble PP without its deposition. The molecular weight of PP could be controlled by selecting reaction conditions for the electrochemical polymerization in the microreactor. In addition, the role of trimethylsilyl (TMS) group in this reaction process was clarified by the comparison to the polymerization of unsubstituted benzene.

1. Introduction

π-Conjugated polymers are regarded as important advanced materials due to their lightness, flexibility, conductivity, and photoelectric properties.1,2 In addition, monodisperse π-conjugated polymers have been developed as simple model systems to mimic the more complex features of the respective π-conjugated polymers owing to well-defined and uniform molecular structure of monodisperse π-conjugated polymers. Under this background, the synthetic chemistry of monodisperse π-conjugated polymers has also developed in the past decades and been subject to diversification in terms of objectives and methods.3 However, conventional methods for the synthesis of monodisperse π-conjugated polymers are mostly based on cross-coupling polycondensation using transition metal catalysts.4 However, these synthetic methods have several disadvantages, such as multi-step requirements, long reaction times, difficulty in developing continuous large-scale processes, and the use of toxic transition metal catalysts. On the other hand, very recently, we have developed a simple and effective method for the synthesis and molecular weight control of poly(3-hexylthiophene) (P3HT) using electro-oxidative polymerization in a flow microreactor.5,6 This synthetic method enabled the control of molecular weight and distribution of the synthesized P3HT by careful selection of the reaction conditions. In addition, the electro-oxidative polymerization was conducted in a flow operation without any oxidants and toxic metal catalysts. Thus, this synthetic method possesses many characteristics designed to overcome the disadvantages of conventional methods for the synthesis of monodisperse π-conjugated polymers.

Polymerization of benzene which is a highly symmetric monomer usually yields the corresponding polymer with backbones comprised of α-, p-, and m-phenylene units.7,8 In addition, such irregular structures influence their physico-chemical properties because of interrupted regularity in the chain. Therefore, not only molecular weight control but also site-selective polymerization is an important research subject for the polymerization of symmetric monomers like benzene. Indeed, many studies have been made to conduct site-selective polymerization so far. Several groups reported that the introduction of trimethylsilyl (TMS) group into the aromatic monomers enabled dominant coupling at α-positions in the electro-oxidative polymerization.9−12 However, Sampath and Loh reported a contradicting finding, that is, TMS group provided steric hinderance to prohibit coupling at α-positions.13

Under these backgrounds, in the present work, we have demonstrated the electro-oxidative polymerization of benzene monomers with and without TMS group introduction in a flow microreactor in order to achieve the molecular weight control of PP and clarify the role of TMS group in the polymerization process.

2. Experimental

2.1 Instrumentation

Electrochemical polymerization was carried out with a Galvosstat (Hokuto Denko HABF-501A). HPLC and GPC analyses were performed with a LC pump (Shimadzu LC-20AD), a UV detector (Shimadzu SPD-20A), and columns (Kanto Kagaku Mightysil Si 60 250-4.6 for HPLC analyses and Showa Denko GPC K-802.5 for GPC analyses). Both chromatograms were recorded by a LC workstation (Shimadzu LabSolutions DB).

2.2 Materials

All reagents were purchased from commercial supplier and used

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with further purification. 1,4-bis(trimethylsilyl)benzene and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) were purchased from Sigma Aldrich. Acetonitrile, toluene, dichloromethane, and sodium sulfate were purchased from Kanto Chemical Co. Trifluoromethanesulfonic acid was purchased from Tokyo Chemical Industry. Standard polystyrene samples of molecular weight 162 (PL2012-1001) and 580 (PL2012-2001) were purchased from Agilent Technologies. Standard polystyrene samples of molecular weight 1.20 × 10³, 2.60 × 10³, and 7.35 × 10³ (Shodex standard SM-105) were purchased from Showa Denko.

### 2.3 Calculation

Geometric structures of 1,4-bis(trimethylsilyl)benzene was optimized using the most popular Becke’s three-parameter hybrid functional, B3,14 with non-local correlation of Lee-Yang-Parr, LYP, abbreviated as B3LYP method.15 This method, based on Density Functional Theory (DFT) for a uniform electron gas (local spin density approximation), is used with the 6-31G (d) basis set.16 An open-shell spin-unrestricted formalism was used for radical cation structure with unpaired electron (UB3LYP). Calculation was carried out with Gaussian 16 Revision A.03.

### 2.4 Flow microreactor

Figure 1 shows schematic illustration of the electrochemical flow microreactor. The reactor was constructed from two Pt plates (3 cm width, 3 cm length). A spacer (80 µm thickness double faced adhesive tape) was used to leave a rectangular channel exposed, and the two electrodes were simply sandwiched together (area of the two electrodes: 1 × 3 cm²). After connecting Teflon tubing to inlet and outlet, the reactor was sealed with epoxy resin.

### 2.5 General procedure for electrochemical polymerization of 1,4-bis(trimethylsilyl)benzene using a flow microreactor

KdScientific model 100 syringe pumps were used to pump the reaction solutions. The solution containing 1,4-bis(trimethylsilyl)benzene (50 mM) in 100 mM tetrabutylammonium hexafluorophosphate/acetonitrile (20 mL) was introduced into the reactor. Constant current electrolyses were performed using the electrochemical flow microreactors composed of Pt plate electrodes (active electrode area, 1 × 3 cm²). The electrolytic solution ejected from the reactor was collected, and acetonitrile solvent was removed by evaporation under reduced pressure. Then, the residue was dissolved in dichloromethane and subjected to column chromatography on silica gel (Kanto Chem. Co., Silica Gel 60 N, spherical, neutral, 63–210 µm) in order to remove supporting electrolyte. Subsequently, the resulting solution was analyzed using HPLC to determine the conversion of 1,4-bis(trimethylsilyl)benzene. The average molecular weights and the molecular weight distribution. The average molecular weights were calibrated with a polystyrene standard.

### 2.6 General procedure for electrochemical polymerization of 1,4-bis(trimethylsilyl)benzene using a batch-type reactor

Electrochemical polymerization of 1,4-bis(trimethylsilyl)benzene (50 mM) was performed using Pt plate anode (working electrode, 2 × 2 cm²) and Pt plate cathode (working electrode, 2 × 2 cm²) in 100 mM Bu₄NPF₆/acetonitrile (30 mL) in a beaker type glass cell (50 mL capacity) equipped with a magnetic stirrer. Electrolysis was conducted with a constant current mode (25.0 mA cm⁻²) by passing 2 F mol⁻¹ of electricity. After the electrolysis, acetonitrile solvent was removed by evaporation under reduced pressure. Then, the residue was dissolved in dichloromethane and subjected to column chromatography on silica gel (Kanto Chem. Co., Silica Gel 60 N, spherical, neutral, 63–210 µm) in order to remove supporting electrolyte. Subsequently, the solution was analyzed using HPLC to determine the conversion of 1,4-bis(trimethylsilyl)benzene.

### 2.7 General procedure for desilylation of the obtained polymers and evaluation of its coupling positions by IR analysis

After the procedure 2.4, the obtained polymer was desilylated with trifluoromethanesulfonic acid to afford unsubstituted PP by the procedure described in Ref.17. In brief, to a 50 mL flask was added silyl-substituted polymer (25 mg), trifluoromethanesulfonic acid (0.1 mL) and toluene (10 mL). After stirred at r.t. for 2 h, the reaction mixture was transferred into a 100 mL separatory funnel, and washed with distilled water (20 mL × 2) and brine (20 mL). The organic layer was dried over sodium sulfate, and the removal of solvent gave unsubstituted PP. To evaluate the coupling positions, the unsubstituted PP were compressed into KBr pellets and analyzed with an FT-IR spectrometer (Shimadzu IRAffinity-1; Shimadzu Corp, Kyoto, Japan).

### 3. Results and Discussion

In general, the electro-oxidative polymerization mechanism can be considered as sequences of coupling of radical cations and deprotonation reaction, so that the bond formation takes place between atoms with high spin density on the monomer radical cation.18 Hence, in the first, we have conducted DFT calculation for the radical cation of 1,4-bis(trimethylsilyl)benzene. As shown in Fig. 2, it was found that the largest spin density was distributed on the C atoms at ipso-position to the trimethylsilyl group. According to this fact, it may be expected that the electro-oxidative polymerization of 1,4-bis(trimethylsilyl)benzene would proceed as sc-
The average molecular weight and polydispersity of polyphenylene obtained by electropolymerization using a batch-type reactor and flow microreactor.

### Table 1. The average molecular weight and polydispersity of polyphenylene obtained by electropolymerization using a batch-type reactor and flow microreactor.

| Reactor type          | Monomer conversion (%) | Average molecular weight | |   |
|-----------------------|------------------------|--------------------------|---|---|
|                       |                        | $M_n$   | $M_w$   | $M_w/M_n$ |   |
| Batch-type reactor    | 55                     | N/A     | N/A     | N/A       |   |
| Flow microreactor     | 54                     | 585     | 704     | 1.20      |   |

*Experimental conditions: anode, Pt plate; cathode, Pt plate; current density, 25.0 mA cm$^{-2}$; flow rate, 28.0 mL h$^{-1}$; electricity, 2.0 F mol$^{-1}$; solvent, acetonitrile; substrate; 50 mM of 1,4-bis(trimethylsilyl)benzene, supporting electrolyte, 100 mM of Bu$_4$NPF$_6$.

*Determined by HPLC.

*Determined by GPC.

Next, to precisely control the molecular weight of PP, the influence of electricity on the average molecular weight and polydispersity of PP in the electro-oxidative polymerization was investigated. For constant-current electro-oxidative polymerization in a flow microreactor with fixed channel dimensions, electricity can be controlled by changing the flow rate. As shown in Table 2, the molecular weight of polymer products increased with an increase in the electricity (caused by a decrease in the flow rate). These results confirmed that the molecular weight of PP could be controlled simply by changing the electricity.

### Table 2. Influence of electricity on the average molecular weight and polydispersity of polyphenylene obtained by electropolymerization using a flow microreactor.

| Conditions of electrolysis | Monomer conversion (%) | Average molecular weight |
|---------------------------|------------------------|--------------------------|
| Flow rate / mL h$^{-1}$   | Electricity / F mol$^{-1}$ | $M_n$ | $M_w$ | $M_w/M_n$ |
| 5.6                       | 10                     | 72    | 708   | 1.20      |
| 11.2                      | 5.0                    | 69    | 680   | 1.24      |
| 18.7                      | 3.0                    | 55    | 659   | 1.16      |
| 28.0                      | 2.0                    | 54    | 585   | 1.20      |

*Experimental conditions: anode, Pt plate; cathode, Pt plate; current density, 25.0 mA cm$^{-2}$; solvent, acetonitrile; substrate; 50 mM of 1,4-bis(trimethylsilyl)benzene, supporting electrolyte, 100 mM of Bu$_4$NPF$_6$.

*Determined by HPLC.

*Determined by GPC.
In the last stage of the investigation, we evaluated the coupling position of PP products by IR spectroscopy after the desilylation with trifluoromethanesulfonic acid (Fig. 3(A)). For comparison, the polymer sample obtained by the electro-oxidative polymerization of benzene was also subjected to IR analysis (Fig. 3(B)). Ibuki et al. performed IR measurements on an extensive library of PPs, and revealed that the prominent bands due to C–H out-of-plane deformation vibrations appeared in the 675–870 cm\(^{-1}\) range (Fig. 3(B)). The band at above 800 cm\(^{-1}\) can be assigned to the absorption of \(p\)-substituted rings and the other bands are corresponded to mono-, ortho-, and meta-rings. As shown in Fig. 3, the intensities of these bands differ apparently in the spectra of both samples. Especially, it can be seen that the peak belonging to \(para\)-substitution is more intense for the sample polymerized with unsubstituted benzene monomer compared to that for the sample prepared with 1,4-bis(trimethylsilyl)benzene monomer. From these results, it can be stated that the use of 1,4-bis(trimethylsilyl)benzene as a monomer inhibited dominant coupling at \(para\)-position in the electro-oxidative polymerization, and TMS group played as the \(alpha\)-coupling inhibitor rather than the \(alpha\)-coupling promotor.

4. Conclusion

Electrochemical synthesis and molecular weight control of well-defined PP were demonstrated using a flow microreactor. The electrochemical flow microreactor allowed effective synthesis of a soluble \(pi\)-conjugated polymer such as PP without polymer deposition. The molecular weight distribution of PP synthesized in the microreactor was preferably narrow, and the molecular weight could be controlled by selecting the reaction conditions for the electro-oxidative polymerization. In addition, IR analyses of the PP samples prepared by the electro-oxidative polymerization of benzene monomers with and without TMS group introduction revealed that TMS group played as the \(alpha\)-coupling inhibitor rather than the \(alpha\)-coupling promotor in the present reaction system.

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