# Chapter IV

発光性ポリ(*p*-フェニレンビニレン)–アミロース複合体の合成

Synthesis of Luminescent

Poly(*p*-phenylenevinylene)-Amylose Composites

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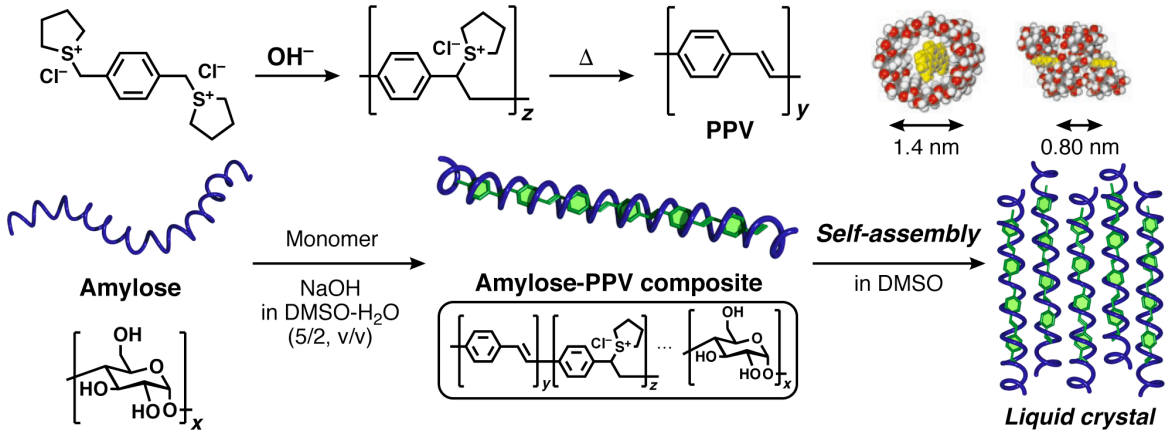
## 1. Introduction

Poly(*p*-phenylenevinylene) (PPV) is the first $\pi$-conjugated polymer used as the emissive layer in light-emitting diodes (LEDs). However, PPV is insoluble in solvents, and therefore a two-step synthesis is required to fabricate the PPV thin films for LEDs. In this experiment, an alternative approach will be considered to synthesize PPV. PPV can be encapsulated in amylose during the polymerization of *p*-xylene-bis(tetrahydrothiophenium) dichloride in aqueous media at ambient temperature (*ca*. 20–25 °C). Thus, one can obtain a soluble, PPV-based luminescent polymer composite.




### 2-1. Synthesis of PPV–amylose composite [1]

Add 68 mg of starch derived from corn and 7 mL of dimethyl sulfoxide (DMSO) to two 50 mL Erlenmeyer flasks, respectively. Put the flasks in a water bath (>70 °C) and stir the solution until the starch completely dissolves (*ca*. 30 min). Add 3 mL of $H_2O$ to each flask by a pipette. After cooling the solution to room temperature, add 16 mg of *p*-xylene-bis(tetrahydrothiophenium) dichloride to the flasks. Shine a UV light toward the solution and check whether or not luminescence can be observed. Observe the solution color, and take a picture if necessary. Stir and cool the solution to 0 °C in an ice water bath. Initiate the reaction by adding 190 μL of 1 M NaOH aqueous solution to each flask using a micropipette.

Quench each reaction by the following procedure.

**Procedure 1:** After 15 min, quench the reaction by adding 200 μL of 1 M HCl using a micropipette.

**Procedure 2:** After 15 min, remove the ice water bath and keep stirring at room temperature for 30 min. Quench the reaction by adding 200 μL of 1 M HCl using a micropipette.

Shine a UV light toward each solution and check whether or not luminescence can be observed. Observe the solution color, and take a picture if necessary. Pour each solution into a 500 mL beaker (transfer all precipitates in the flask by a glass rod). Add 200 mL of acetone to the solution. Filtrate each solution by a filter paper. Wash the residue with 15 mL of methanol followed by 15 mL of acetone. Place the collected sample in a desiccator and dry *in vacuo* at room temperature for 30 min. Weigh the obtained amylose-PPV composite and record the yield. Hereafter, the products obtained through Procedure 1 and Procedure 2 will be called as compound **1** and compound **2**, respectively.

**2-2. Preparation of a polymer film (compound 1 and compound 2)**

Place 2 mg of each compound (compound **1** and compound **2**) on a microscope slide. Cast 2–3 drops of DMSO to each compound and then rub each DMSO mixture with a spatula. Dry each film *in vacuo* at room temperature overnight.

**3. Synthesis of PPV without amylose**

Add 16 mg of *p*-xylene-bis(tetrahydrothiophenium) dichloride and 7 mL of DMSO to a 50 mL Erlenmeyer flask. Add 3 mL of $H_2O$ by a pipette. Shine a UV light toward the solution and check whether or not luminescence can be observed. Observe the solution color and take a picture if necessary. Stir and cool the solution to 0 °C in an ice water bath. Initiate the reaction by adding 190 μL of 1 M NaOH aqueous solution using a micropipette. After 15 min, remove the ice water bath and keep stirring at room temperature for 30 min.

Quench the reaction by adding 200 μL of 1 M HCl using a micropipette. Shine a UV light toward the solution and check whether or not luminescence can be observed (take a picture if necessary). Pour the solution into a 500 mL beaker (transfer all precipitates in the flask by a

glass rod). Add 200 mL of acetone to the solution. Filtrate the solution by a filter paper. Wash the residue with 15 mL of methanol followed by 15 mL of acetone. Place the sample in a desiccator and dry *in vacuo* at room temperature for 30 min (compound **3**). Weigh the product and record the yield.

**4. Measurements**

**4-1. UV-Vis measurement**

Prepare a 0.5 mg/mL polymer solution in DMSO for each product (compound **1**–**3**). Filter the solution and put it in a 1 cm disposable cell to measure the UV-Vis spectrum.

**4-2. Photoluminescence (PL) measurement**

Dilute each solution of the samples prepared in Section 4-1 so that the absorbance of their UV-Vis peaks at longest wavelength becomes ca. 0.05. Remove oxygen from the solution by bubbling with $N_2$ gas. Measure the excitation and emission spectra for each dilute solution as well as the films (compound **1** and compound **2**) prepared in Section 2-2.

**Reference**

1. Ikeda, M.; Furusho, Y.; Okoshi, K.; Tanahara, S.; Maeda, K.; Nishino, S.; Mori, T.; Yashima, E. A Luminescent Poly(phenylenevinylene)–Amylose Composite with Supramolecular Liquid Crystallinity. *Angew. Chem., Int. Ed.* **2006**, *45*, 6491–6495.

## レポート作成上の注意

1. 様式は特に指定しないが、緒言・実験操作と結果・考察を A4 版のレポート用紙 4 枚以内にまとめること。ただし、表紙は含めない。
2. 実験操作はフローチャート式に整理すること。
3. 試薬の使用量・収量・収率・融点・固体の形状などを正確に記入すること。
4. その他、各段階での考察は、気づいた点や失敗した点などを含め、実験操作と結果の次に詳しく記入すること。また、本テーマについての総合的な考察を最後に必ず記入すること。特に以下の点を必ず考察に含めること。
   ・フィルム状態と溶液状態での蛍光スペクトルの違い
   ・Corn starch の有無および反応時間の違いによる各種スペクトルの違い