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A Luminescent Poly(phenylenevinylene)–Amylose Composite with Supramolecular Liquid Crystallinity

Masato Ikeda, Yoshio Furusho, Kento Okoshi, Sayaka Tanahara, Katsuhiro Maeda, Shunsuke Nishino, Tatsuo Mori, and Eiji Yashima**

Poly(*p*-phenylenevinylene) (PPV) is the first π-conjugated polymer used as the emissive layer in light-emitting diodes (LEDs).[1] However, PPV is insoluble in solvents, and therefore a two-step synthesis is required for the fabrication of the PPV thin films for LEDs; the synthesis of a solution-processable precursor polymer **2** by polymerization of the disulfonium salts of α,α′-dichloro-*p*-xylene (**1**), followed by thermal conversion of the precursor to the PPV film at high temperature (Figure 1 a).[1,2] To improve its processability, numerous soluble PPV derivatives have been synthesized by a side-chain functionalization.[3] Another attractive alternative is "encapsulation or wrapping" of conjugated polymers by organic hosts through noncovalent bonding interactions, thus leading to soluble and processable insulated molecular wires.[4] Cyclodextrins[5] and polysaccharides, such as amylose[6] and schizophyllan,[4c,6c,d,7] have been extensively used for these purposes. They possess a chiral hydrophobic cavity that forms inclusion complexes or polyrotaxanes with soluble conjugated polymers[4,6c,d,7] and carbon nanotubes[6a,b] that fit the cavity size in solution.[4b,8] However, the wrapping approach cannot be applicable to PPV because it is totally insoluble and intractable. Herein, we demonstrate that PPV can be encapsulated in amylose during the polymerization of monomer **1** in aqueous media at ambient temperature (ca. 20–25 °C), thus resulting in a soluble, PPV-based lumi-

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[*] Dr. M. Ikeda, Dr. Y. Furusho, Dr. K. Okoshi, Prof. E. Yashima
Yashima Super-structured Helix Project
Exploratory Research for Advanced Technology (ERATO)
Japan Science and Technology Agency (JST)
101 Creation Core Nagoya, Shimoshidami
Moriyama-ku, Nagoya 463-0003 (Japan)
Fax: (+81) 52-739-2081
E-mail: furusho@yp-jst.jp
yashima@apchem.nagoya-u.ac.jp
Homepage: http://helix.mol.nagoya-u.ac.jp/
http://helix.mol.nagoya-u.ac.jp/

S. Tanahara, Dr. K. Maeda, Prof. E. Yashima
Department of Molecular Design and Engineering
Graduate School of Engineering, Nagoya University
Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3185

S. Nishino, Prof. T. Mori
Department of Electrical Engineering and Computer Science
Graduate School of Engineering, Nagoya University
Chikusa-ku, Nagoya 464-8603 (Japan)

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

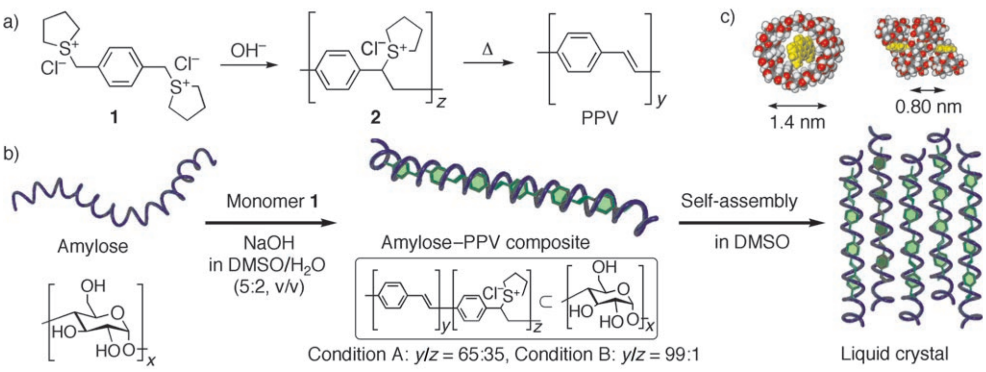

Figure 1. a) Scheme showing the synthesis of PPV. b) Schematic illustration of the synthesis of a green-luminescent amylose–PPV composite, which further self-assembles into a molecular ordering in LC phases. Condition A: NaOH (1 M), DMSO/H_2O (5:2 v/v; [NaOH]/[amylose] = 4:1) at room temperature for 30 min; Condition B: NaOH (1 M), DMSO/H_2O (5:2 v/v; [NaOH]/[amylose] = 10:1) at 0 °C for 0.5 h and then at 20 °C for 48 h. c) Calculated structure of amylose (15 glucose units)–PPV (3 mer) shown using a space-filling model in the top (left) and side (right) views; PPV yellow, amylose red, white, and gray.

nescent polymer composite (Figure 1 b). Moreover, amylose, which is too flexible to form a liquid crystal (LC),[9] exhibits an liquid crystallinity when the PPV is threaded into the amylose tube, thereby resulting in a rigid-rod supramolecular assembly.

The amylose–PPV composites were synthesized by polymerization of monomer **1** (5 mM) in a mixture of dimethyl sulfoxide (DMSO) and alkaline water (5:2 v/v; [NaOH]/[**1**] = 4:1) in the presence of amyloses (45 mM based on the glucose units; molecular weight (M_W) = 15 000, 24 000, and 50 000 with a polydispersity index (PDI) of 1.05).[10] The polymerization proceeded homogeneously at 25 °C and quantitatively produced the luminescent composites (92–95 % yield) within 30 minutes without heat treatment after quenching the reaction with aqueous HCl followed by precipitation into acetone (condition A).[11] The resulting composites are soluble in water and organic solvents and show typical absorption and photoluminescence (PL) spectra in water (3 % DMSO) as a result of the conjugated phenylenevinylene (PV) units (see Supporting Information), but the solution ^1H and solid-state ^{13}C NMR spectra of the composites (see Figure 2 and Supporting Information)[11] suggest that the core polymer contains approximately 35 mol % of the precursor units.[12] Further heat treatment of the amylose–PPV composites in DMSO/water (5:2 v/v) at 100 °C for 4 hours did not improve the PV content because of the intermolecular cross-linking between the remaining reactive precursor units and the OH groups of amylose inside the cavity (see Supporting Information).

The amylose–PPV composites are quite stable as evidenced by the size-exclusion chromatography (SEC) analyses (see Supporting Information). Three amyloses with different molecular weights showed unimodal SEC curves detected only by a refractive index (RI), whereas the amylose–PPV composites exhibited similar SEC curves detected by both the RI and visible light (400 nm); the molecular-weight distribution remained unimodal, thus indicating that the PPV cores hardly unthread from the tube, even in the absence of stoppers at the ends.[5a–e] These SEC results also support the proposed structure (Figure 1 b), in which the PV segments are encapsulated in the amylose cavity.

To decrease the defect (precursor units), we investigated the effects of the polymerization temperature (0–30 °C), time (0.5–48 h) and the concentrations of amylose (45–90 mM), **1** (5–10 mM), and NaOH ([NaOH]/[**1**] = 4:1–20:1 (molar ratio)) on the content of PV units in the resulting polymer composites, from which we determined the optimized conditions. We found that the polymerization of **1** (5 mM) in DMSO/alkaline water (5:2 v/v; [NaOH]/[**1**] = 10:1) in the

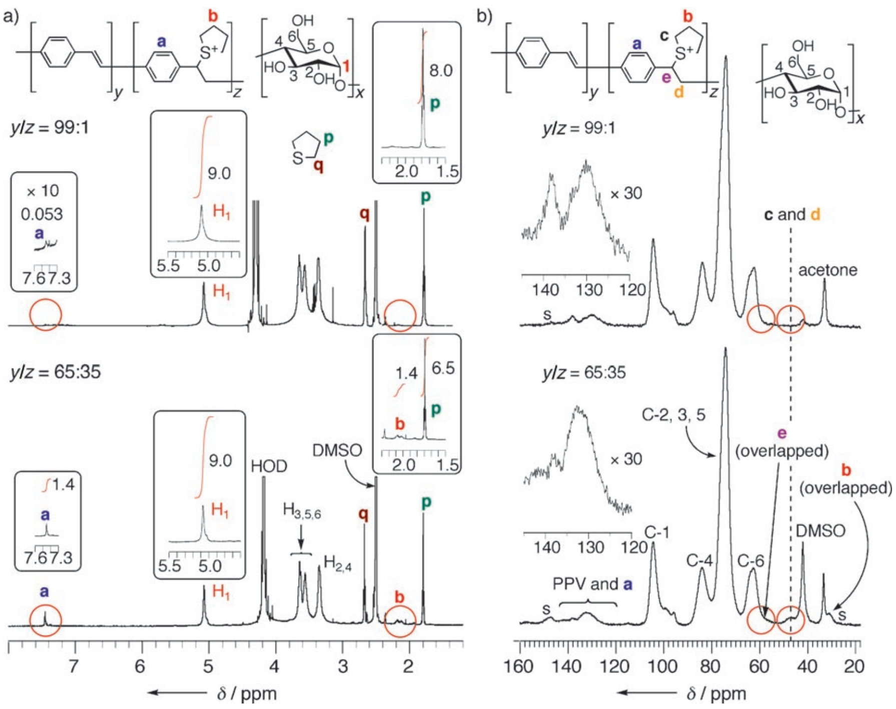

Figure 2. a) ^1H NMR spectra ([D$_6$]DMSO/D_2O (5:2 v/v), 25 °C) of the polymerization mixtures under condition A (bottom) and B (top) after addition of 1 M DCl. b) ^{13}C CP–MAS NMR spectra of the amylose (15 000)–PPV composites prepared under condition A (bottom) and B (top) measured at 5.5 kHz at 25 °C. s = spinning side bands.

presence of amylose (45 mM) at 0 °C for 30 min and then at 20 °C for 48 h quantitatively gave an almost defect-free amylose–PPV composite (99 % PV units and [glucose units of amylose]/[PV] = 9:1) based on its solution ^{1}H and solid-state ^{13}C NMR spectra and elemental analysis (see Figure 2 and Supporting Information).[12,14] The solid-state ^{13}C NMR resonance peak pattern that arose from the PV part at around $\delta = 120$–140 ppm (see Figure 2 b and Supporting Information) and the absorption spectral pattern and the maximum wavelengths in the PL spectra (509 and 544 nm; Figure 3) for the amylose–PPV composite obtained under the optimized condition (condition B) are similar to those of a typical PPV reported previously.[15] The Raman spectrum of the composite film also supports the structure of PPV (see Supporting Information); the composite exhibited characteristic Raman bands that result from the stretching vibration of the vinyl groups (1328 and 1626 cm^{-1}) and phenyl rings (1173, 1548, and 1585 cm^{-1}) of the PV units. The intensity ratio of the C=C stretching vibration of the phenyl ring (1585 cm^{-1}) and vinyl group (1626 cm^{-1}; I_{1548}/I_{1626}) is higher than one with excitation at 785 nm, thus suggesting that the conjugation segment of the PPV in the amylose–PPV composite appears to be long for a typical PPV.[16]

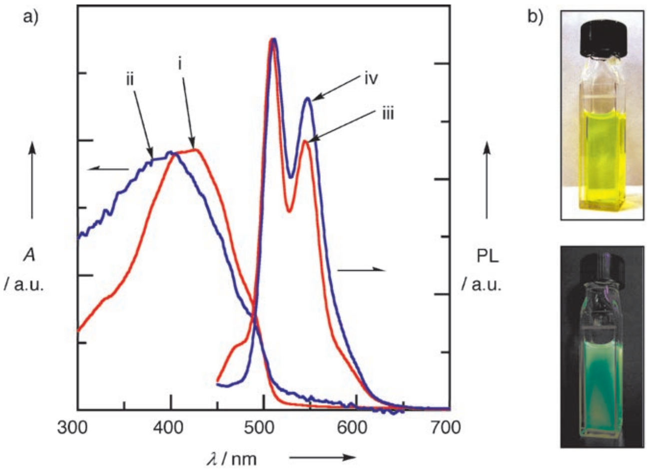

Figure 3. a) Absorption (i, ii), photoluminescence (excitation wavelength = 425 (iii) and 400-nm (iv)) spectra of the amylose (24 000)–PPV composite prepared under condition B in DMSO (1.0 (i) and 0.1 mg mL^{-1} (iii) red trace) and in the film state (ii, iv) blue trace. b) Photographs of the amylose (24 000)–PPV composite under white (top) and UV light at 365 nm (bottom).

The mechanism of the in situ encapsulation of PPV in the amylose tube during the polymerization of **1** in DMSO/alkaline water and the structure of the composites have not been clearly elucidated so far, but a possible mechanism can be proposed as follows: First, monomer **1** generates, through base catalysis, an intermediate quinodimethane species, which then polymerizes to produce the water-soluble sulfonium precursor oligomer or polymer **2**.[17] These species are too hydrophilic to be included in the hydrophobic amylose interior.[8,18] We, therefore, consider that once the precursor polymer or oligomer is generated in DMSO/alkaline water, part of the precursor units may be converted into the luminescent PV segments, which are highly hydrophobic and immediately entrapped in the hydrophobic amylose tube. These conversion and encapsulation processes may be accelerated in the presence of amylose and/or DMSO with excess NaOH, as any soluble PPVs could not be detected by photoluminescence in the absence of amylose or in the presence of maltohexaose and β-cyclodextrin under the identical polymerization conditions. According to this mechanism, the amylose–PPV composite containing 35 mol % of the precursor units prepared under condition A may have a random distribution of the two segments, which may further slowly convert into the PPV segments in the presence of excess NaOH.

Amylose is known to adopt a left-handed helix with a 0.8-nm pitch of six glucose units per turn in aqueous solution (see Figure 1 c and Supporting Information).[8,18] Combined with computer modeling, a sixfold amylose of $M_w = 15\,000$ (93 glucose units) can be calculated to accommodate approximately 18 PV units. The obtained amylose (15 000)–PPV composite ([glucose]/[PV] = 9:1) may be able to accommodate approximately 11 PV units, but when the feed molar ratio increased during the polymerization, the amylose–PPV composite precipitated and became insoluble. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of PPVs obtained by acid hydrolysis of the amylose (15 000)–PPV composites (conditions A and B) showed a molecular-mass distribution that ranged from approximately 500 to 1600 Da, which corresponds to a 5 mer to 14 mer of PV units (see Supporting Information).

Biological[19] and synthetic[20] rigid-rod helical polymers often form lyotropic LCs, but helical amylose shows no LC phases as a result of an overall flexible-chain characteristic in solution and films.[9] However, we anticipated that when a stiff, rodlike polymer is threaded into the flexible amylose tube, the resulting complex might become a rigid-rod, thus showing LCs in concentrated solutions. Figure 4 a shows a polarizing optical micrograph of the amylose (24 000)–PPV composite prepared under the optimized conditions in a concentrated solution of DMSO (ca. 60 wt %). The observed Schlieren-like texture suggests a typical LC of nematic order. The reason why the optically active amylose-based complexes did not show a chiral LC such as a cholesteric LC is not clear at present.[21] An analogous nematic order occurs in colloidal solutions of the biological tobacco mosaic virus.[22] The solution of higher-molecular-weight amylose (50 000)–PPVs in DMSO (ca. 50 wt %; conditions A and B) also showed a similar nematic LC (see Supporting Information). Films prepared by solvent evaporation of the solutions of the amylose–PPVs in DMSO on a Teflon sheet and fibers that showed a green luminescence (Figure 4 b and c) retained their molecular ordering, as evidenced by the polarizing optical microscopy (Figure 4 d).

In summary, we have synthesized the first water-soluble, luminescent PPV-based polymer composite by polymerization of the precursor monomer in aqueous media in the presence of amylose. PPV encapsulated in an amylose tube can be further processed into luminescent films and fibers. Moreover, amylose, which is too flexible to form an LC,

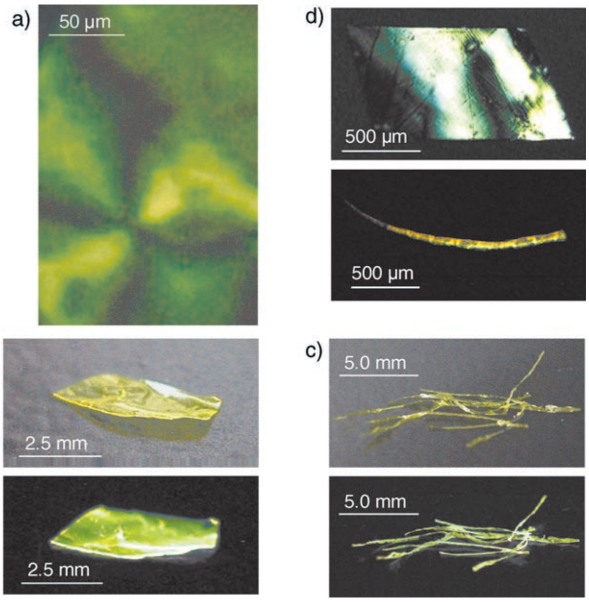

Figure 4. a) Polarizing optical micrograph of approximately 60 wt% solution of the amylose (24000)–PPV in DMSO. Photographs of an amylose–PPV b) film and c) fiber under white (top) and UV light at 365 nm (bottom). d) Polarizing optical micrographs of the amylose–PPV film (top) and fiber (bottom) are also shown.

exhibits an LC when the PPV is threaded into the amylose tube, thus resulting in a rigid-rod assembly. This supramolecular liquid-crystal formation is conceptually new and the polymer lengths of the amylose can be controlled by using the enzymatic polymerization technique.[10] Therefore, this approach will provide luminescent PPV-based amyloses with controlled molecular lengths and aspect ratios and will promise access to potentially valuable optoelectronic, chiral, and biocompatible materials with a controlled molecular order.

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[11] See Supporting Information for details of the synthesis, structures, and characterization of the amylose–PPV composites.

[12] The molar proportion of amylose (x), the PV part (y), and the precursor part (z) was estimated from the ^{1}H NMR spectra during the in situ polymerization of **1** in the presence of amylose in [D$_6$]DMSO/D$_2$O (5:2 v/v; Figure 2a). The proportion was estimated based on the relative peak integrals of the signal H_1 of amylose, the phenyl signal H_a of the precursor part, and the released tetrahydrothiophene signal H_p after the polymerization, as the signals that arose from the PV part were greatly broadened, presumably as a result of its restricted motion on encapsulation in the amylose tube; hence, the signals of the PV part could not be used for the estimation. The molar proportions of the PV part relative to the precursor part were calculated to be 65:35 and 99:1 for the composites prepared under conditions A and B, respectively.[11] In the ^{13}C CP–MAS NMR spectra (B), the absence of the precursor part in the amylose (15000)–PPV composite obtained under condition B (top) was confirmed from the disappearance of a broad signal at around $\delta = 40$–50 ppm as a result of the precursor part (c and d; bottom).[13] We note that the peak pattern from the PV part at around $\delta = 120$–140 ppm for the amylose (15000)–PPV composite obtained under condition B (top) is similar to that of a typical PPV previously reported.[13]

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