Chemical Modification of a Luminescent Poly(phenylenevinylene)-Amylose Composite

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Introduction

Poly(*p*-phenylenevinylene) (PPV) has attracted a great deal of interest due to its potential applications as polymeric organic light-emitting diodes (OLEDs), organic solar cells, and conducting materials.[1] However, PPV is totally insoluble in solvents and infusible due to its rigid-rod structure of the main chain. Therefore, in order to fabricate PPV thin films for OLEDs, a two-step synthesis is required; a soluble precursor polymer was first prepared and then thermally converted to the PPV films at a high temperature.[1a,2] Since then, numerous soluble and processable PPV derivatives, such as poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), have been synthesized to improve the solubility of PPV by polymerization of the corresponding monomers bearing various flexible substituents.[3]

Recently, we found that the PPV could be encapsulated in amylose during the polymerization of *p*-xylenebis(tetrahydrothiophenium) dichloride in an aqueous media and the resulting luminescent amylose-PPV composite (APPV) was soluble in dimethyl sulfoxide (DMSO), and further self-assembled into a liquid crystalline phase.[4] Since this approach enabled us to fabricate an APPV film through a one-step solution process, the APPV film was employed as the emitting layer in the OLEDs, and their properties were investigated.[5] The photoluminescence efficiency of the APPV film was improved in comparison to that of the typical PPV film probably due to the inhibition of the fluorescence quenching between the stacked PPV molecules and prevention of the exciton migration by wrapping the PPV with insulative amylose.[6] Although a green light was illuminated from the device, the maximum luminance of the APPV-based OLED was not so high (52 cd/m^2).[5] The conductance of the APPV films appeared to decrease from that of a naked PPV film due to wrapping the conductive PPV by a large insulative amylose molecule. In addition, the APPV is only soluble in high-boiling solvents, such as DMSO and aqueous DMSO, so that it was difficult to make a smooth and uniform thin film without cracks and void suitable for OLEDs.

Amylose has reactive hydroxy groups, and we anticipated that a chemical modification of the exterior amylose encapsulating PPV might enhance the solubility of the APPV and further improve its photo- and electro-luminescence efficiencies. In this study, we performed the chemical modification of APPV by introducing various substituents, such as long alkyl chains and/or functional groups having an electron-transporting ability into the hydroxy groups of the exterior amylose through macromolecular reaction. We show that the APPV composites remain intact and encapsulate the PPV within its helical cavity after the chemical modification of the amylose to form highly soluble and processable PPV-based luminescent polymer composites.

Results and Discussion

An almost defect-free APPV composite (phenylenevinylene unit/precursor unit = 99/1 (mol/mol)) was prepared according to the previously reported method.[4] In order to improve the solubility of the APPV, the hydroxy groups of the amylose were first allowed to react with octyl isocyanate ([octyl isocyanate]/[OH groups of amylose] = 0.6 (mol/mol)) in *N*,*N*-dimethylacetamide− (DMA−) pyridine (8/5, v/v) in the presence of a small amount of lithium chloride (LiCl) at 90 °C for 24 h[7] as outlined in Scheme 1A. The resulting modified APPV with octyl isocyanate through carbamate linkages (O-APPV) was soluble in DMSO and mostly soluble in tetrahydrofuran (THF) (ca. 76%). The THF-soluble O-APPV contained ca. 30 mol% of octyl carbamate residues as estimated by its ^{1}H NMR spectrum and elemental analysis (see Supporting Information). A smooth and uniform thin film could be fabricated by spin casting a THF solution of O-APPV without difficulty and the film showed a green luminescence under UV light at 365 nm (Figure 1B.) The absorption and photoluminescence spectra of O-APPV in THF and in the film state (Figure 1A) are similar to those of the original APPV[4] as well as a typical PPV reported previously[8] except for the relatively large shoulder peak at around 460 nm in THF. These results indicate that the APPV could be chemically modified with octyl isocyanate to produce a soluble and easy-processable PPV-based luminescent polymer composite, while maintaining the conductive PPV encapsulated in the amylose cavity.[9]

The introduction of such long alkyl chains to the amylose enhanced the solubility of APPV, but may reduce the conductance of APPV when used as the emitting layer in the OLEDs because of a further increase in the intermolecular distance between the conductive PPV segments encapsulated in the insulative amylose. We then performed the chemical modification of APPV with acetic anhydride to introduce shorter chains than the octyl groups to the amylose. The acetylated APPV (A-APPV) was prepared according to Scheme 1B. The A-APPV obtained after the reaction with an excess amount of acetic anhydride in DMA-pyridine (8/5, v/v) in the presence of a small amount of LiCl at 65 °C for 36 h was completely soluble in THF and contained ca. 90 mol% of acetyl groups as estimated by its ^{1}H NMR spectrum and elemental analysis (see Supporting Information).[10] Figure 2A shows the absorption and photoluminescence spectra of A-APPV in THF. These spectral patterns are also similar to those of the original APPV, suggesting that the APPV retains its inclusion structure even after most of the hydroxy groups of the amylose were converted to the acetates.[9,11]

As described above, the conductance of the APPV films appears to decrease as compared with that of a naked PPV film due to the wrapping by insulative amylose. We anticipated that

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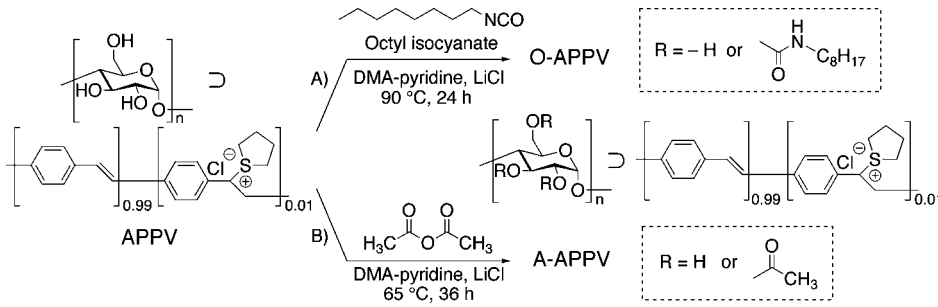
Scheme 1. Synthesis of APPV Derivatives Modified with Octyl Isocyanate (O-APPV) and Acetic Anhydride (A-APPV)



the carrier balance could be improved by the introduction of an electron-transporting substituent, such as an oxadiazole group, to APPV because PPV is well-known to be a hole-transporting material, so that the introduction of the oxadiazole groups might increase in the conductance of the APPV composite. We then designed and synthesized a novel oxadiazole derivative bearing an isocyanate group (**4**) as outlined in Scheme 3 (see Experimental Section) and performed the chemical modification of APPV with **4** to introduce the electron-transporting oxadiazole units into the hydroxy groups of the exterior amylose through the carbamate linkages. The APPV was allowed to react with **4** in DMA-pyridine (8/5, v/v) ([**4**]/[OH groups in APPV] = 0.15) in the presence of LiCl at 90 °C for 24 h (Scheme 2.) The obtained composite modified with **4** (OXD-APPV) was soluble in DMSO, but insoluble in THF. Therefore, the OXD-APPV was further modified with octyl isocyanate ([octyl isocyanate]/[OH groups in APPV] = 0.6) in the same way for O-APPV in order to increase its solubility. A THF-soluble composite modified with both oxadiazole and octyl groups through carbamate linkages (OXD-OAPPV) was obtained after the removal of a THF-insoluble part (ca. 34%) by filtration. The contents of the oxadiazole and octyl carbamate units were estimated to be ca. 7 and 25%, respectively, from its ^{1}H NMR spectrum. Figure 2B shows the absorption spectra of OXD-OAPPV in THF and APPV in DMSO. The peak at around 304 and 417 nm can be assigned to the oxadiazole and PV units, respectively, and the OXD-OAPPV showed a strong blue luminescence in THF under UV irradiation (365 nm) due to the emission from the oxadiazole units (inset in Figure 2). These results demonstrate that different substituents can be introduced onto the hydroxy groups of the exterior amylose by stepwise macromolecular reactions, while retaining its inclusion structure.

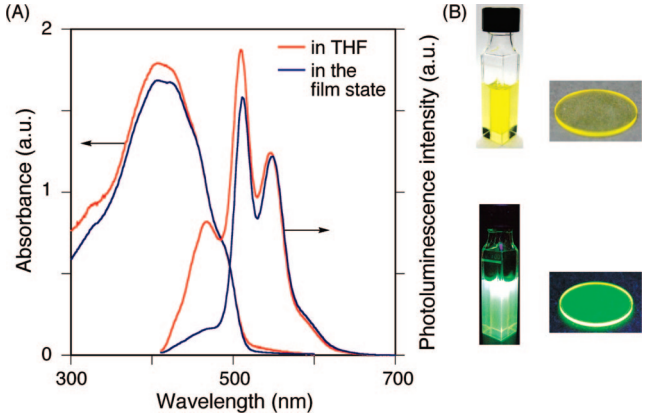


Figure 1. (A) Absorption and photoluminescence (excitation wavelength = 406 nm) spectra of O-APPV in THF (red lines) and in the film state (blue lines). (B) Photographs of O-APPV in THF and in the film state under white (top) and UV light at 365 nm (bottom).

As reported previously, APPV formed a supramolecular lyotropic liquid crystal (LC) phase in a concentrated DMSO solution due to the rigid-rod PPV encapsulated in a flexible amylose tube.[4] The modified APPV composites also formed similar lyotropic LC phases in concentrated THF (O-APPV and OXD-OAPPV) and chloroform (A-APPV) (Figure 3) as anticipated.

In summary, we have synthesized a variety of THF-soluble, luminescent PPV-based amylose composites by chemical modification of the amylose. The PPV-based modified amylose composites maintained its characteristic supramolecular liquid crystallinity and rotaxane-like structure even after modification of the exterior amylose. The present results suggest that the desired functional groups can be introduced into the composites, which have a great advantage, such that the thin films suitable for more efficient and processable emitting layers in the OLEDs

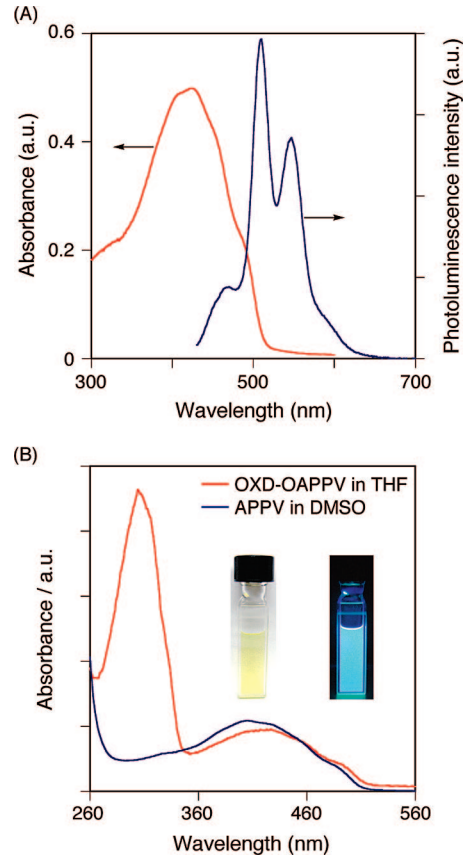
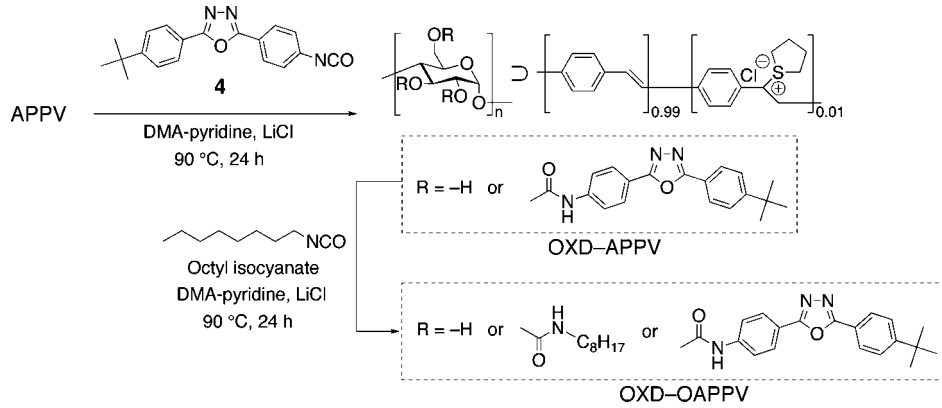
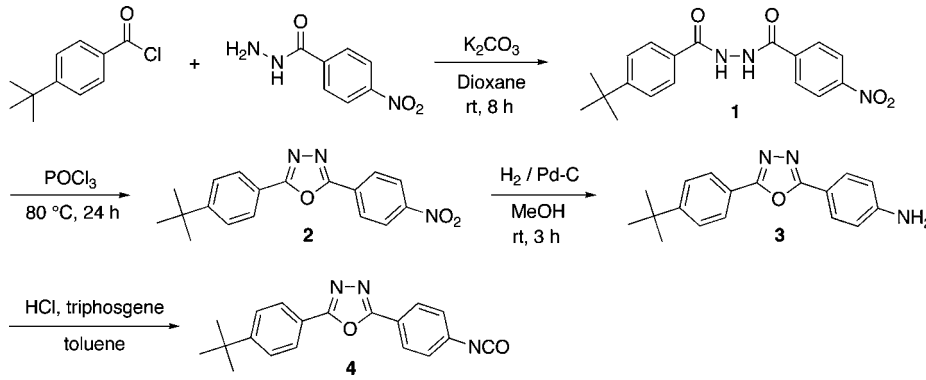


Figure 2. (A) Absorption (red line) and photoluminescence (blue line) (excitation wavelength = 426 nm) spectra of A-APPV in THF. (B) Absorption spectra of OXD-OAPPV in THF (red line) and APPV in DMSO (blue line). Inset shows the photographs of OXD-OAPPV in THF under white (left) and UV light at 365 nm (right).

Scheme 2. Synthesis of APPV Derivatives Modified with Oxadiazole Derivative and Octyl Isocyanate (OXD-OAPPV)



Scheme 3. Synthesis of Oxadiazole Derivative Bearing an Isocyanate Group (4)



will be fabricated. A further study along this line is now in progress.

Experimental Section

Instruments. Melting point was measured on a Yanako melting point apparatus and is uncorrected. NMR spectra were taken on a Varian Mercury 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C) or a Varian VXR-500S (500 MHz for ^{1}H) spectrometer in $CDCl_3$ or DMSO-d_6 using TMS (for $CDCl_3$, ^{1}H and ^{13}C) or a solvent residual peak (for DMSO-d_6, ^{1}H and ^{13}C) as the internal standards. IR spectra were recorded with a JASCO Fourier Transform IR-620 spectrophotometer (Hachioji, Japan). The absorption and photoluminescence spectra were measured in a 1.0-mm or 1.0-cm quartz cell on a JASCO V-570 spectrophotometer and a JASCO FP 6500 spectrofluorometer, respectively. The polarizing optical microscopic observations were performed using a Nikon Eclipse E600 POL polarized microscope (Tokyo, Japan) equipped with a DS-5 M CCD camera connected to a DS-L1 control unit (Nikon). Elemental analyses were performed by the Nagoya University Analytical Laboratory in School of Bioagricultural Sciences.

Materials. Anhydrous DMA, pyridine, 1,4-dioxane, methanol (water content <0.005%), and toluene (water content <0.003%) were purchased from Wako (Osaka, Japan). Anhydrous DMSO (water content <0.005%) was obtained from Aldrich (Milwaukee, WI). THF was dried over sodium benzophenone ketyl and distilled under nitrogen. These solvents were stored under nitrogen. Amylose (MW 15,000) with $M_w/M_n = 1.98$ and triphosgene were purchased from Tokyo Kasei (TCI, Tokyo, Japan). Acetic anhydride and LiCl were obtained from Kishida (Osaka, Japan). Palladium-activated carbon (Pd/C, 5 wt%) and octyl isocyanate (97%) were available from Aldrich. Phosphoryl chloride ($POCl_3$) was from Wako. Oxadiazole derivative (**4**) was prepared according to Scheme 3.

***N′*-(4-*tert*-Butylbenzoyl)-4-nitrobenzohydrazide (1).** To a solution of 4-nitrobenzoic hydrazide (9.1 g, 50 mmol) and potassium carbonate (6.6 g, 48 mmol) in dioxane (200 mL) was added a solution of 4-*tert*-butylbenzoyl chloride (9.8 mL, 78 mmol) in dioxane (50 mL). The reaction mixture was stirred at room temperature for 8 h under nitrogen. After the addition of 1 N HCl aqueous solution (250 mL) to the reaction mixture, the precipitated white solid was collected by filtration and washed two times with water and dried *in vacuo* at room temperature overnight, yielding 17.8 g of **1** in 99% yield. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ 10.85 (br s, NH, 1H), 10.58 (br s, NH, 1H), 8.38 (d, $J = 6.9$ Hz, aromatic, 2H), 8.15 (d, $J = 6.9$ Hz, aromatic, 2H), 7.87 (d, $J = 8.5$

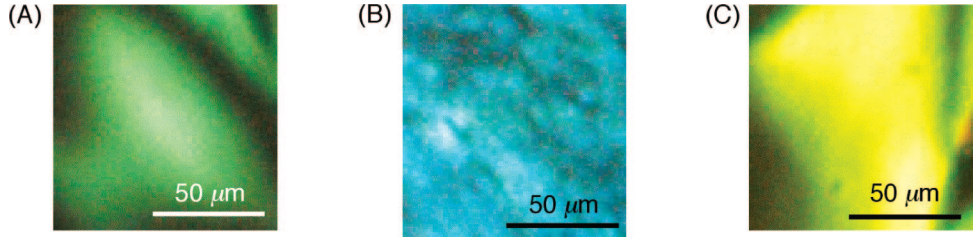


Figure 3. Polarized optical micrographs of lyotropic LC phases of O-APPV (A) and OXD-OAPPV (B) in THF and A-APPV (C) in chloroform.

Hz, aromatic, 2H), 7.54 (d, J = 8.5 Hz, aromatic, 2H), 1.32 (s, *tert*-butyl, 9H).

2-(4-*tert*-Butylphenyl)-5-(4-nitrophenyl)-1,3,4-oxadiazole (2). A solution of compound **1** (10 g, 29 mmol) in $POCl_3$ (50 mL) was stirred under a nitrogen atmosphere at 80 °C overnight. After the solution was allowed to cool to room temperature, the solution was poured into ice−water (300 mL). The white precipitate was collected by filtration and washed thoroughly with acetone and dried *in vacuo* at room temperature overnight to give 6.4 g of **2** in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.41 (d, J = 8.5 Hz, aromatic, 2H), 8.34 (d, J = 8.6 Hz, aromatic, 2H), 8.09 (d, J = 8.3 Hz, aromatic, 2H), 7.58 (d, J = 8.5 Hz, aromatic, 2H), 1.39 (s, *tert*-butyl, 9H).

2-(4-Aminophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (3). To a suspension solution of compound **2** (1.00 g, 3.09 mmol) in dry methanol (40 mL) was added Pd/C (320 mg) under nitrogen. The mixture was stirred at room temperature for 3 h under a hydrogen atmosphere. After filtration through Celite, the solvent was removed under reduced pressure to give pure **3** as a white powder in 97% yield (0.88 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.04 (d, J = 8.8 Hz, aromatic, 2H), 7.93 (d, J = 8.6 Hz, aromatic, 2H), 7.53 (d, J = 8.8 Hz, aromatic, 2H), 6.77 (d, J = 8.8 Hz, aromatic, 2H), 4.07 (s, NH_2, 2H), 1.37 (s, *tert*-butyl, 9H).

2-(4-*tert*-Butylphenyl)-5-(4-isocyanatophenyl)-1,3,4-oxadiazole (4). The hydrochloride of compound **3** was prepared by bubbling hydrochloric acid gas generated from the reaction of concentrated sulfuric acid with concentrated hydrochloric acid into a dry toluene solution (20 mL) of **3** (0.70 g, 2.39 mmol). A solution of triphosgene (1.64 g, 5.54 mmol) in toluene (20 mL) was added dropwise to the suspended solution of the hydrochloride of **3** in toluene. The reaction mixture was stirred at 80 °C until no starting material was detected by IR spectroscopy. After purging with nitrogen in order to remove any unreacted phosgene gas, the precipitate was removed by filtration. The solvent was then removed under reduced pressure to give pure **4** as a white powder in 51% yield (391 mg). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 8.11 (d, J = 2.0, 6.8 Hz, aromatic, 2H), 8.06 (d, J = 2.0, 6.3 Hz, aromatic, 2H), 7.56 (dd, J = 2.0, 6.5 Hz, aromatic, 2H), 7.25 (dd, J = 1.5, 6.0 Hz, aromatic, 2H), 1.38 (s, *tert*-butyl, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 165.02, 163.81, 155.78, 128.52, 127.03, 126.35, 125.72, 121.72, 121.11, 35.36, 31.26. IR (KBr, cm^{-1}): 2263 ($\nu_{N=C=O}$).

Synthetic Procedure for Modified APPV with Octyl Isocyanate (O-APPV). APPV (50 mg, 0.86 mmol), which had been prepared according to the previously reported method,[4] was dispersed in DMA-pyridine (8/5, v/v, 10 mL) containing LiCl (15.9 mg, 0.36 mol) at 80 °C under nitrogen, and octyl isocyanate (0.10 mL, 0.57 mmol) was then added dropwise to the mixture. After being stirred at 90 °C for 24 h, the reaction mixture was cooled to room temperature and then poured into a large amount of diethyl ether and the resulting yellow precipitate was collected by centrifugation, washed with diethyl ether, and dried *in vacuo* at room temperature overnight to give O-APPV. The obtained O-APPV contained a THF-insoluble part (15.0 mg), which was removed by centrifugation after dispersing the composite in a small amount of THF. The THF-soluble part was poured into a large amount of water, and the yellow precipitate was collected by centrifugation and dried *in vacuo* at room temperature overnight to give THF-soluble O-APPV in 51% yield (45.7 mg). The content of the octyl carbamate residues in O-APPV was estimated to be approximately 30 mol% by its ^{1}H NMR spectrum in DMSO-d_6 at 60 °C: the peak intensity of the methyl proton resonances of the octyl groups relative to that of the glucose proton resonances of amylose was used. This value satisfied the elemental analysis. Anal. Calcd for $(C_6H_{10}O_5)_{9.00}(C_8H_6)_{0.99}(C_{12}H_{15}ClS)_{0.01}(C_9H_{17}NO)_{8.1}$: C, 57.47; H, 8.36; N, 4.02. Found: C, 57.31; H, 8.48; N, 4.20. IR (KBr, cm^{-1}): 1617 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, DMSO-d_6, 60 °C): δ 6.92−6.80 (br, NH, 1H), 5.51−5.00, 4.53−4.03, 3.83−3.31, 2.96 (m, glucose unit), 1.42 (s, 2H, CH_2), 1.26 (s, 12H, $(CH_2)_6$), 0.87 (s, 3H, CH_3).

Synthetic Procedure for Modified APPV with Acetic Anhydride (A-APPV). APPV (202 mg, 3.46 mmol) was dispersed in DMA−pyridine (8/5, v/v, 20 mL) containing LiCl (34.2 mg, 0.806 mmol) at 50 °C under nitrogen. To this was added dropwise acetic anhydride ([acetic anhydride]/[OH groups in APPV] = 2) (670 mL, 6.91 mmol). After being stirred at 65 °C for 36 h, the solution was allowed to cool to room temperature. After the reaction mixture was concentrated to the half-volume by evaporation, the residue was poured into a large amount of ethanol and the resulting yellow precipitate was collected by centrifugation, washed with ethanol, and dried *in vacuo* at room temperature overnight to give A-APPV in 72% yield (241.0 mg). It contained ca. 90 mol% of acetyl groups as estimated by its ^{1}H NMR spectrum in $CDCl_3$ at 50 °C. This value was in agreement with that estimated by elemental analysis. Anal. Calcd for $(C_6H_{10}O_5)_{9.00}(C_8H_6)_{0.99}(C_{12}H_{15}ClS)_{0.01}(C_2H_2O_1)_{24.3}$: C, 51.42; H, 5.64. Found: C, 51.30; H, 5.56. IR (KBr, cm^{-1}): 1749 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 5.45−5.23, 4.86−4.68, 4.46−3.91, 3.62 (m, glucose unit), 2.18−1.97 (m, 3H, CH_3).

Synthetic Procedure for Modified APPV with Oxadiazole Derivative 4 and Octyl Isocyanate (OXD-OAPPV). APPV (227 mg, 3.90 mmol) was dispersed in DMA-pyridine (8/5, v/v, 40 mL) containing LiCl (68.2 mg, 1.61 mmol) at 80 °C under nitrogen. To this was added dropwise a solution of **4** ([**4**]/[OH groups in APPV] = 0.15) (251 mg, 0.786 mmol) in DMA (5 mL), and the mixture was stirred at 90 °C for 24 h. After the reaction mixture was allowed to cool to room temperature, the mixture was poured into a large amount of diethyl ether and the resulting yellow precipitate was collected by centrifugation, washed with diethyl ether, and dried *in vacuo* at room temperature overnight. The obtained crude product was dissolved in a small amount of DMSO and the solution was then poured into a large amount of acetone to remove the unreacted **4**. The yellow precipitate was collected by centrifugation and dried *in vacuo* at room temperature overnight to give OXD-APPV in 50% yield (158 mg).

The resulting OXD-APPV (130.6 mg, 2.25 mmol) was dispersed in DMA-pyridine (8/5, v/v, 20 mL) containing LiCl (52.7 mg, 1.24 mmol) at 80 °C under nitrogen and octyl isocyanate ([octyl isocyanate]/[OH groups in APPV] = 0.6) (238 mL, 1.35 mmol) was then added dropwise to the mixture. After being stirred at 90 °C for 24 h, the reaction mixture was allowed to cool to room temperature and then poured into a large amount of diethyl ether. The resulting yellow precipitate was collected by centrifugation, washed with diethyl ether, and dried *in vacuo* at room temperature overnight to give OXD-OAPPV (183 mg). Most of the obtained OXD-OAPPV was soluble in THF, but contained a THF-insoluble part (44.8 mg), which was removed by centrifugation after dissolving the composite in a small amount of THF. The THF-soluble part was poured into a large amount of water and the yellow precipitate was collected by centrifugation and dried *in vacuo* at room temperature overnight to give THF-soluble OXD-OAPPV in 45% yield (87.3 mg). The contents of the oxadiazole and octyl carbamate units were estimated to be ca. 7 and 25%, respectively, from its ^{1}H NMR spectrum in DMSO-d_6 at 80 °C. These values were in agreement with those estimated by elemental analysis. Anal. Calcd for $(C_6H_{10}O_5)_{9.00}(C_8H_6)_{0.99}(C_{12}H_{15}ClS)_{0.01}(C_{19}H_{17}N_3O_2)_{1.89}(C_9H_{17}NO)_{6.75}(H_2O)_{16}$: C, 54.42; H, 7.91; N, 4.97. Found: C, 54.20; H, 8.11; N, 5.15. ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 8.00−7.61 (m, aromatic, 8H), 6.75 (br, NH, 1H), 5.48−5.18, 4.51−4.25, 4.03−3.56, 3.17−2.80, (m, glucose unit), 1.41 (s, 2H, CH_2), 1.34 (s, 9H, *t*-Bu), 1.25 (s, 12H, $(CH_2)_6$), 0.86 (s, 3H, CH_3). IR (KBr, cm^{-1}): 1617 ($\nu_{C=O}$).

Polarized Microscopy Studies. A small amount of O-APPV composite (ca. 1 mg) was placed on a slide glass plate and then a small amount of THF (ca. 10 μL) was dropped close to the composite. A cover glass was placed on the sample and the specimen was subjected to polarized optical microscopy observations with a Nikon E-600POL polarized microscope. A clear birefringent texture was observed only at the interface between the isotropic solution and solid states. The concentration of the solution was not determined due to the fast evaporation of the solvents. In

the same way, polarized optical microscopy observations were performed for A-APPV with chloroform and OXD-OAPPV with THF.

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Supporting Information Available: Figure showing the ^{1}H NMR spectra of O-APPV, A-APPV, and OXD-OAPPV. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The inclusion formation of PPV in the modified amylose was supported by the fact that the enzymatic hydrolysis of APPV in an aqueous solution by an aminoglucosidase (EC 3.2.1.3 from *Rhizopus* species, SIGMA) immediately resulted in green luminescent precipitates, which were insoluble in solvents. In the present study, we could not observe such luminescent precipitates during the macromolecular reaction.

(10) When the reaction time was 6 h, the obtained APPV was barely soluble in THF and the content of acetyl groups in the A-APPV, determined by ^{1}H NMR spectroscopy, in DMSO-d_6 was ca. 75%.

(11) It is surprising that the acetylated amylose (A-APPV) could include a large PPV molecule, since the helical structure of amylose significantly changed after the acetylation[12] and an acetylated amylase with a high degree of substituent (DS) possessed a poor inclusion ability toward the organic molecules in water.[13]

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