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Incorporation of π-Conjugated Polymer into Silica: Preparation of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]/Silica and Poly(3-hexylthiophene)/Silica Composites

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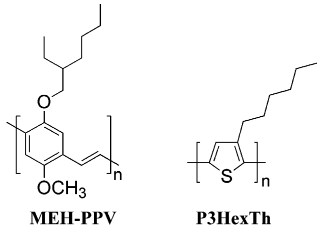
ABSTRACT: The Wittig reaction of 2-methoxy-5-(2-ethylhexyloxy)-*p*-xylylenebis(triphenylphosphonium chloride) with 2-methoxy-5-(2-ethylhexyloxy)benzene-1,4-dicarbaldehyde was carried out to obtain poly-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) terminated with a phosphonium moiety at the chain end. Poly[3-hexylthiophene-*co*-3-(6-hydroxyhexyl)thiophene]s were prepared by regioselective coupling reaction of 2-bromo-3-hexylthiophene and 2-bromo-3-(6-(2-tetrahydropyranyloxy)-hexyl)thiophene and subsequent cleavage of a tetrahydropyranyl group. Acid-catalyzed polycondensations of tetraethoxysilane (TEOS) were carried out in the presence of these polymers to give homogeneous composites with silica. The resulting composite materials were characterized by UV−vis and emission spectra.

Introduction

Organic/inorganic composite materials have rapidly become a fascinating new field of research in materials science. The sol−gel method is widely studied for obtaining an organic/silica composite which combines the advantages of the organic molecule (flexibility, prosessability, ductility) and the inorganic material (rigidity, high thermal stability).[1,2] A three-dimensional silica network can be formed by a stepwise polycondensation reaction of alkoxysilane. Its low-temperature processing allows organic molecule to be incorporated into silica without decomposition. We are interested in the incorporation of π-conjugated polymer into silica because π-conjugated polymers are a class of materials that hold promise as a basis for electrooptical applications. Although π-conjugated polymer/silica composites have attracted particular interest, its preparation is severely limited by the incompatibility of the two components. Several laboratories have reported the incorporation of π-conjugated polymers into silica. Poly-(1,4-phenylenevinylene)s/silica composites have been successfully prepared by the sol−gel method using water/alcohol-soluble sulfonium salt precursors.[3−6] Wei et al. reported polyaniline/silica composite using the sol−gel method of poly[methyl methacrylate-*co*-3-(trimethoxysilyl)propyl methacrylate] in the presence of camphorsulfonic acid-doped polyaniline.[7]

This report describes another approach for preparing π-conjugated polymer/silica composites employing the sol−gel method. Our idea is to introduce polar functional groups into π-conjugated polymers in order to improve the compatibility between the polymer and silica. The interaction between the functional group of the polymer and silanol group of silica during sol−gel process is expected to help a homogeneous composite formation.

Scheme 1



In this study poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly(3-hexylthiophene) (P3HexTh) have been chosen as representative soluble π-conjugated polymers (Scheme 1). We introduced phosphonium salt moiety and hydroxy group onto MEH-PPV and P3HexTh, respectively. Preparations and optical properties of MEH-PPV/silica and P3HexTh/silica composites will be reported.

Experimental Section

Materials. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and butyllithium were purchased from Aldrich and used as received. Tetraethoxysilane (TEOS) was distilled under reduced pressure. Tetrahydrofuran (THF) was purified by distillation over sodium under nitrogen using benzophenone as an indicator for dryness. Diisopropylamine was distilled from sodium hydroxide under nitrogen. *N*-Bromosuccinimide (NBS) was recrystallized from boiling water. All other reagents were purchased from Tokyo Kasei Kogyo (TCI) and used without further purification. Merck silica gel (grade 60, 70−230 mesh) was used for column chromatography.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a JEOL EX-270 nuclear magnetic resonance at 270 and 67.5 MHz, respectively. Samples were dissolved in $CDCl_3$, and tetramethylsilane (TMS) was added as the internal standard. Infrared spectra were recorded on a Jasco IR-700 infrared spectrophotometer. Gel permeation chromatography (GPC) was carried out on a Tosoh HLC-8020 chromatograph equipped with polystyrene gel columns (Tosoh G2500H + G3000H; exclusion limit = 6×10^4; 300 × 7.5 mm)

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and refractive/ultraviolet dual mode detectors. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using polystyrene standards. UV−vis spectra were recorded on a Jasco Ubest V-570 spectrophotometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with exciting wavelength of 365 nm. Elemental analysis was performed on a Yanaco MT-5 CHN CORDER.

Diethyl 2,5-Bis(5-hexenyloxy)terephthalate (2). A mixture of diethyl 2,5-dihydroxyterephthalate[8] (**1**) (32.4 g, 9.5 mmol), 6-bromo-1-hexene (3.4 g, 21 mmol), potassium carbonate (87.3 g, 53 mmol), and 80 mL of *N,N*-dimethylformamide (DMF) was stirred at 80 °C for 20 h. The reaction mixture was poured in water and extracted with ethyl acetate. The organic layer was washed with water three times, dried over anhydrous magnesium sulfate, and placed under reduced pressure to give 2.8 g (69%) of **2** as a yellow oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.34 (s, 2H), 5.9−5.7 (m, 2H), 5.1−4.9 (m, 4H), 4.37 (q, $J = 7.3$ Hz, 4H), 4.01. ^{13}C NMR ($CDCl_3$, δ, ppm): 166.0, 151.6, 138.4, 124.7, 116.5, 114.7, 69.5, 61.2, 33.3, 28.7, 25.2, 14.2. IR (NaCl, ν, cm^{-1}): 1731 (C=O). Anal. Calcd for $C_{24}H_{34}O_6$: C, 68.88; H, 8.19. Found: C, 68,57; H, 8.10.

2,5-Bis(5-hexenyloxy)-*p*-xylylene Alcohol (3). Into a suspension of lithium aluminum hydride (0.55 g, 15 mmol) in 40 mL of ether was added diester **2** in 40 mL of ether, and the mixture was heated under reflux for 1 h. The reaction mixture was cooled to 0 °C, and water was added dropwise to the solution. The mixture was extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and placed under reduced pressure to remove the solvent to give 2.0 g (82%) of **3** as white needles. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.85 (s, 2H), 5.9−5.7 (m, 2H), 5.1−4.9 (m, 4H), 4.67 (d, $J = 6.6$ Hz, 4H), 3.99 (t, $J = 6.3$ Hz, 4H), 2.31 (t, $J = 6.6$ Hz, 2H), 2.13 (q, $J = 6.9$ Hz, 4H), 1.9−1.7 (m, 4H), 1.7−1.5 (m, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 150.6, 138.4, 129.1, 114.9, 112.3, 8.5, 62.0, 33.3, 28.8, 25.3. IR (KBr, ν, cm^{-1}): 3292 (O−H). Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.99; H, 8.95.

2,5-Bis(5-hexenyloxy)benzene-1,4-dicarbaldehyde (4). To a stirred suspension of pyridinium chlorochromate (PCC) (1.9 g, 8.9 mmol) and sodium acetate (0.49 g, 6.0 mmol) in 100 mL of dichloromethane was added a solution of diol **3** (2.0 g, 6.0 mmol) in 20 mL of dichloromethane at room temperature. After 12 h, the mixture was filtered through Florisil (magnesium silicates), and the solvent was evaporated at reduced pressure. The residue was purified by silica gel column chromatography (eluent: dichloromethane) to give 0.87 g (44%) of dialdehyde **4** as a yellow solid: mp 55 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 10.50 (s, 2H), 7.43 (s, 2H), 5.9−5.7 (m, 2H), 5.1−4.9 (m, 4H), 4.10 (t, $J = 6.3$ Hz, 4H), 2.14 (q, $J = 7.3$ Hz, 4H), 1.9−1.8 (m, 4H), 1.7−1.5 (m, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 189.2, 138.1, 129.2, 115.0, 111.6, 69.0, 33.3, 28.4, 25.2. IR (KBr, ν, cm^{-1}): 1713 (C=O). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.40; H, 7.25.

2-Methoxy-5-(2-ethylhexyloxy)-1,4-bis(diethoxyphosphinylmethyl)benzene (6). A mixture of 2-methoxy-5-(2-ethylhexyloxy)-*p*-xylylene chloride[9] (2.8 g, 8.4 mmol) and triethyl phosphite (2.8 g, 17 mmol) was heated at 160 °C for 3 h. After cooling, the reaction mixture was charged on a silica gel column using ethyl acetate as the eluent. After the first band was collected, the eluent was changed to a mixture of dichloromethane and methanol (8:2 by volume), and the second band was collected to give 3.8 g (85%) of **6** as an orange oil. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.91 (s, 2H), 4.1−3.8 (m, 12H), 3.22 (d, $J = 20.5$ Hz, 4H), 1.8−1.6 (m, 6H), 1.5−1.2 (m, 46H), 0.88 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR ($CDCl_3$, δ, ppm): 150.5, 150.4, 119.2, 119.0, 114.5, 113.6, 70.9, 61.6, 61.5, 55.8, 39.4, 30.3, 28.8, 23.6, 22.7, 16.0, 13.6, 10.8. IR (NaCl, ν, cm^{-1}): 1219 (P=O).

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene-*co*-2,5-bis(5-hexenyloxy)-1,4-phenylenevinyllene] (7). Into a solution of **4** (179 mg, 0.59 mmol), 2-methoxy-5-(2-ethylhexyloxy)benzene-1,4-dicarbaldehyde[10] (**5**) (618 mg, 2.11 mmol), and **6** (1.451 g, 2.70 mmol) in 15 mL of THF was added potassium *tert*-butoxide (0.62 g, 8.1 mmol) at room temperature. The reaction mixture was heated under reflux for 20 h and poured into methanol to precipitate the polymer. It was dissolved in a small amount of THF, and the resulting solution was poured into methanol to precipitate the polymer again. This procedure was repeated twice to give 0.11 g (77%) of **7** as a red powder: ^{1}H NMR ($CDCl_3$, δ, ppm): 7.7−6.7 (phenyls and vinylene), 5.9−5.7 (−CH=), 5.1−4.8 (CH_2=), 4.1−3.7 (OCH_2), 3.6−3. (CH_3O), 1.9−0.8 (CH, CH_2, and CH_3). GPC (THF eluent, polystyrene standard): $M_n = 17\,000$ Da.

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene-*co*-2,5-bis(6-triethoxysilylhexyloxy)-1,4-phenylenevinylene] (8). A mixture of polymer **7** (1.0 g), triethoxysilane (1.7 g, 10 mmol), hydrogen hexachloroplatinate(IV) hexahydrate (10 mg), and 16 mL of dichloromethane was heated under reflux for 60 h. The reaction mixture was diluted with dichloromethane and filtered. The filtrate was placed under reduced pressure to remove the solvents to give 1.2 g (quant) of **8** as a red powder: ^{1}H NMR ($CDCl_3$, δ, ppm): 7.7−6.7 (phenyls and vinylene), 4.1−3.7 (OCH_2), 3.6−3. (CH_3O), 1.9−0.8 (CH, CH_2, and CH_3). GPC (THF eluent, polystyrene standard): $M_n = 17\,000$ Da.

Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (10). To a stirred solution of an equimolar amount of dialdehyde **5** (200 mg, 0.670 mmol) and 2-methoxy-5-(2-ethylhexyloxy)-*p*-xylylenebis(triphenylphosphonium chloride)[11] (**9**) (576 mg, 0.670 mmol) in a mixture of 3 mL of ethanol and 2 mL of chloroform was added dropwise a solution of 176 mg (2.6 mmol) of sodium methoxide dissolved in 3 mL of ethanol at room temperature under nitrogen. The reaction mixture was stirred for 24 h and poured into methanol to precipitate the polymer. It was washed well with methanol to give 150 mg (44%) of **10** as a red powder. GPC (THF eluent, polystyrene standard): $M_n = 10\,200$ Da.

3-(6-(2-Tetrahydropyranyloxy)hexyl)thiophene (13). A solution of 6-chlorohexyl 2-tetrahydropyranyl ether[12] (**11**) (9.6 g, 45 mmol) in 15 mL of THF was added to magnesium ribbons (1.1 g, 45 mmol). After completion of the addition, the mixture was heated under reflux for 12 h. To the Grignard solution was added [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride (0.23 g, 0.38 mmol) and a solution of 3-bromothiophene (**12**) (6.2 g, 38 mmol) in 10 mL of THF at 0 °C. The mixture was then heated under reflux for 12 h. After cooling, the reaction mixture was poured into ammonium chloride solution and extracted with ether. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was distilled under reduced pressure to give 7.3 g (72%) of **13** as a colorless liquid: bp 160−161 °C/2 mmHg. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.3−7.1 (m, 1H), 7.0−6.8 (m, 2H), 4.6−4.5 (m, 1H), 3.9−3.3 (m, 4H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.9−1.3 (m, 14H). ^{13}C NMR ($CDCl_3$, δ, ppm): 143.1, 128.2, 125.0, 119.8, 98.8, 67.6, 62.3, 30.7, 30.5, 30.2, 29.7, 29.1, 26.1, 25.5, 19.7. Anal. Calcd for $C_{15}H_{24}O_2S$: C, 67.21; H, 9.01. Found: C, 67.40; H, 8.89.

2-Bromo-3-(6-(2-tetrahydopyranyloxy)hexyl)thiophene (14). A mixture of **13** (2.6 g, 9.7 mmol), *N*-bromosuccinimide (NBS) (1.8 g, 10 mmol), 6 mL of acetic acid, and 6 mL of chloroform was stirred at 50 °C for 30 min. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with NaOH solution until pH ~6, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The crude product was purified by silica gel column chromatography (eluent: dichloromethane) to give 1.6 g (48%) of **14** as a yellow liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.18 (d, $J = 6.4$ Hz, 1H), 6.79 (d, $J = 6.4$ Hz, 1H), 4.6−4.5 (m, 1H), 3.9−3.3 (m, 4H), 2.62 (t, $J = 7.6$ Hz, 2H), 1.9−1.3 (m, 14H). ^{13}C NMR ($CDCl_3$, δ, ppm): 141.8, 128.1, 125.1, 108.8, 98.8, 67.5, 62.3, 30.7, 29.6, 29.5, 29.3, 29.0, 26.0, 25.5, 19.6. Anal. Calcd for $C_{15}H_{23}BrO_2S$: C, 51.87; H, 6.67. Found: C, 51.99; H, 6.83.

Poly[3-hexylthiophene-*co*-3-(6-(2-tetrahydropyranyloxy)hexyl)thiophene] (16). In a typical example, 4.1 mL of 1.6 M *n*-butyllithium in hexane (6.5 mmol) was added to a solution of diisopropylamine (0.66 g, 6.5 mmol) in 30 mL of THF at −78 °C. The solution was warmed to 0 °C, stirred for 5 min, and cooled back at −78 °C. To this reaction mixture was added a solution of 2-bromo-3-hexylthiophene[12] (1.26 g,

Table 1. Preparation of MEH−PPV/Silica Composite

run	MEH-PPV (mg)	TEOS (mL)	THF (mL)	acid (mL)	additive (mL)	appearance
1	10	4	6	2 M HCl (1)	none	phase separated
2	5	4	6	1 M HCl (1)	none	phase separated
3	5	4	6	1 M HCl (1)	DMF (1)	phase separated
4	1	4	6	1 M HCl (1)	DMF (1)	phase separated
5	1	4	6	0.1 M HCl (1)	DMF (2)	phase separated

5.1 mmol) and **14** (0.44 g, 1.3 mmol) in 5 mL of THF and the solution was stirred at −78 °C for 40 min. This mixture was cooled to −60 °C, magnesium bromide diethyl etherate (1.67 g, 6.5 mmol) was added, and then the reaction mixture was stirred at −40 °C for 20 min. The reaction mixture was slowly allowed to warm to 0 °C, and [1,3-bis(diphenylphosphino)-propane]nickel(II) dichloride (17 mg, 0.03 mmol) was added. The mixture was stirred at room temperature for 12 h and poured into methanol to precipitate the polymer. It was further purified by Soxhlet extraction using methanol for 24 h and then hexane for 24 h to remove oligomers. Finally, the polymer was isolated from the remaining residue via Soxhlet extraction with chloroform. The chloroform solution was evaporated to give copolymer **16b** (0.46 g, 39%) as a dark purple solid. GPC (THF eluent, polystyrene standard): $M_n = 9200$ Da.

Poly[3-hexylthiophene-*co*-3-(6-hydroxyhexyl)thiophene] (17). In a typical example, a mixture of **16b** (100 mg), 20 mL of THF, and 1 mL of 10% hydrochloric acid solution was heated under reflux for 24 h. The reaction mixture was poured into methanol to precipitate the polymer to give 90 mg (quant) of **17b** as a red powder. GPC (THF eluent, polystyrene standard): $M_n = 8800$ Da.

Poly(3-hexylthiophene) (P3HexTh). Structurally homogeneous head-to-tail P3HexTh was prepared from 2-bromo-3-hexylthiophene according to the procedure[12] reported by McCullough and co-workers. ^{1}H NMR (CDCl$_3$, δ, ppm): 6.97 (thiophene), 2.9−2.7 (CH$_2$),1.7−1.3 (CH$_2$), 0.9 (CH$_3$). GPC (THF eluent, polystyrene standard): $M_n = 7500$ Da.

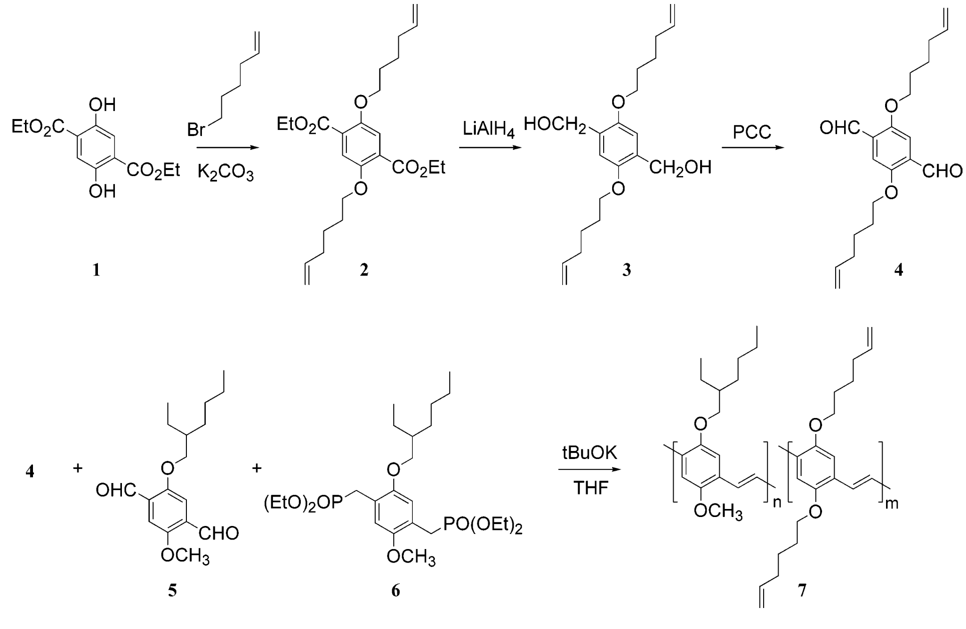
Sol−Gel Method. Given amounts of polymer, tetraethoxysilane (TEOS), 1,4-dioxane or THF, hydrochloric acid, and DMF or dimethyl sulfoxide (DMSO) were mixed with stirring in a polypropylene test tube (15 mm in diameter and 150 mm in length). The tube was set in an oven and heated at 60 °C for 48 h. The temperature was gradually increased to 100 °C and allowed to stand for additional 48 h. Finally, the gel was dried under vacuum to give a solid of cylindrical shape (ca. 6 mm in diameter and ca. 25 mm in length).

Results and Discussion

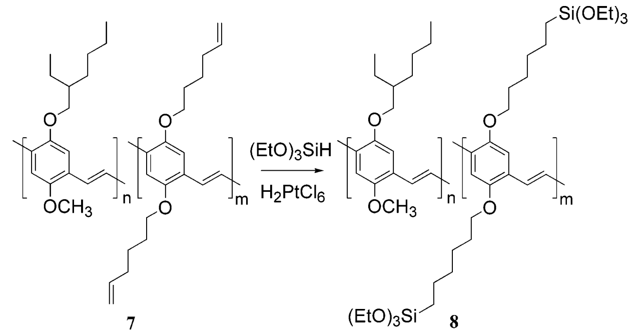
Preparation of MEH−PPV/Silica Composite. A number of different polymers have been incorporated into silica by sol−gel reaction. As a preliminary experiments, we carried out the sol−gel reaction of TEOS in the presence of commercial available MEH-PPV (Aldrich, average M_n: 40 000−70 000). The results are summarized in Table 1. In all runs the organic polymer precipitated during the sol−gel process to give heterogeneous solid. Obviously, this is due to the lack of any physical or chemical interactions between organic component and inorganic material.

To prevent phase separation during the sol−gel process, Chujo and co-workers utilized the formation of the covalent bonds between organic polymers and inorganic phase. They prepared triethoxysilyl-terminated polyoxazolines and carried out their acid-catalyzed cohydrolysis polymerization with TEOS to produce homogeneous transparent glassy composite materials.[14] The organic polymers are covalently attached to the silica network. From this background information, we designed a triethoxysilyl-functionalized MEH-PPV. 2,5-Bis(5-hexenyloxy)benzene-1,4-dicarbaldehyde (**4**) was prepared from diethyl 2,5-dihydroxyterephthalate (**1**) according to Scheme 2. Then, we carried out the Horner−Emmons reaction between 2-methoxy-5-(2-ethylhexyloxy)-1,4-bis(diethoxyphosphinylmethyl)-benzene (**6**) and 2-methoxy-5-(2-ethylhexyloxy)benzene-1,4-dicarbaldehyde (**5**) in the presence of **4** to obtain precursor polymer **7** (Scheme 2). Its ^{1}H NMR spectrum gave a CH peak at 5.9 ppm assigned to terminal vinyl group and a CH$_3$ peak at 3.5 ppm assigned to methoxy group. The composition of the copolymer was determined from the ratio of integrals of these peaks to yield m:n = 81:19, which is consistent with the feed ratio. The hydrosilylation reaction of polymer **7** was carried out in the presence of hydrogen hexachloroplatinate to obtain triethoxysilyl-functionalized MEH-PPV **8** (Scheme 3). Clear pregel solution was obtained by dissolving polymer **8** in a mixture of TEOS and THF. However,

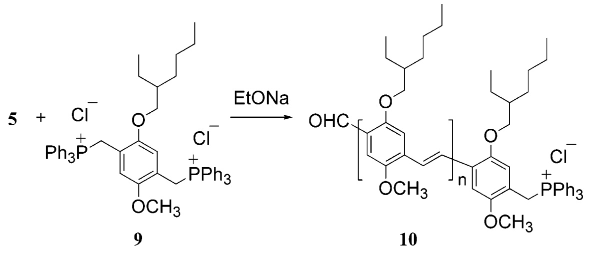
Scheme 2



Scheme 3



Scheme 4



precipitation of the polymer occurred after the addition of hydrochloric acid into the solution to start the polycondensation reaction. This is probably due to the chemical cross-linking reaction of polymers by the intermolecular condensation of triethoxysilyl groups, indicating that the formation of the organic gel is much faster than that of silica gel.

Utilizing ionic interaction between organic polymer and silica is also useful for homogeneous composite formation. To introduce an ionic functional group onto MEH-PPV, Wittig reaction between dialdehyde **5** and diphosphonium salt **9** was carried out to obtain **10** (Scheme 4). Statistically, a MEH-PPV polymer chain prepared by this method has a polar phosphonium salt group at the chain end. The polar group at the chain end is expected to be effective for homogeneous composite formation due to the existence of the electrostatic interaction between phosphonium salt moiety and SiOH groups. The ^{1}H NMR spectrum of **10** is shown in Figure 1. The peaks due to the terminal structures are clearly observed. The peak at 5.5 ppm corresponds to the methylene protons arising from the terminal triphenylphosphoniomethyl group. The existence of two aldehyde peaks (10.4 and 10.5 ppm) can be explained by considering the possible terminal structures as shown in Scheme 5.

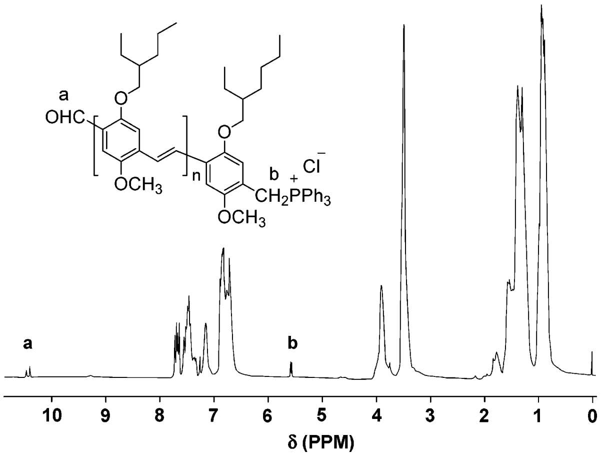
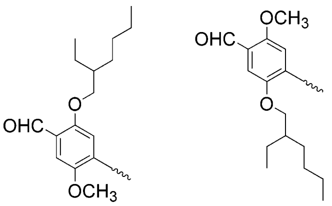


Figure 1. ^{1}H NMR (270 MHz, CDCl$_3$, 25 °C) spectrum of MEH-PPV (**10**) prepared by the Wittig method.

Scheme 5



The acid-catalyzed hydrolysis and polycondensation of TEOS was carried out in the presence of **10**. The results are summarized in Table 2. In all cases, clear transparent composites were obtained. The addition of dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMF) as a drying control additive^{15} was effective to give a crack-free composite (runs 2 and 3). Without such a high boiling point solvent crack formation was observed during the drying process (run 1).

Optical Property of MEH-PPV/Silica Composite. Figure 2 shows UV–vis absorption spectra of pristine MEH-PPV (**10**) in dioxane solution and **10**/silica composite (obtained from run 2 in Table 2). Both spectra exhibited similar absorption spectra and absorption edges, indicating no significant effect on the electronic structure of MEH-PPV after composite formation. The photoluminescence spectra of **10** in dioxane solution and **10**/silica composite are shown in Figure 3. The emission of **10**/silica composite showed similar spectrum to that of **10** in dioxane solution. A slight red shift of the spectrum in silica composite compared with that in diluted solution may be attributed to aggregation or

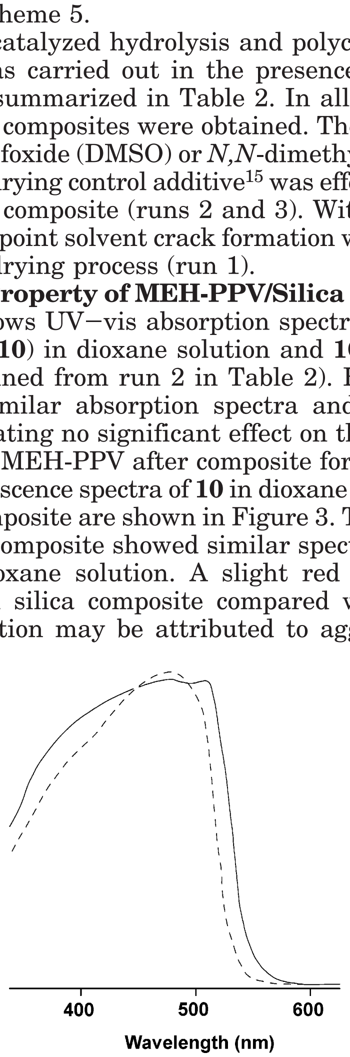


Figure 2. UV–vis spectra of **10** in dioxane solution (dashed line) and **10**/silica composite (solid line).

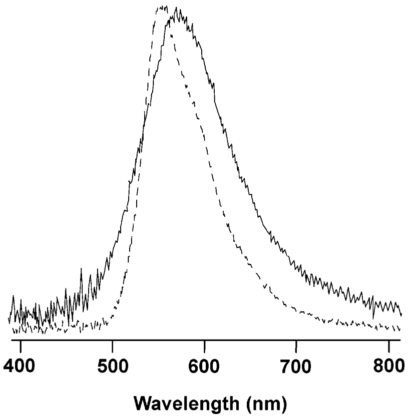
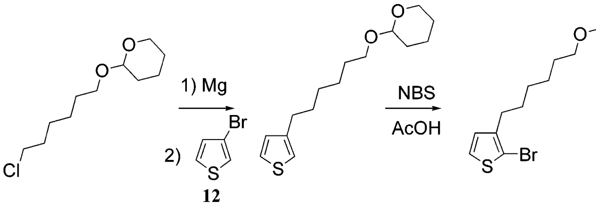


Figure 3. Photoluminescence spectra of **10** in dioxane solution (dashed line) and **10**/silica composite (solid line).

Table 2. Preparation of 10/Silica Composite

run	**10** (mg)	TEOS (mL)	THF (mL)	1 M HCl (mL)	additive (mL)	appearance
1	5	4	6	1	none	transparent
2	5	4	6	1	DMSO (1)	transparent
3	5	4	6	1	DMF (1)	transparent

Scheme 6



11 **12** **13** **14**

interaction of polymer chains. The polymer concentration in the silica composite calculating from the gel volume (ca. 3 mg/mL) is much higher than that in dioxane solution (ca. 0.01 mg/mL). The observed similarities between the spectrum in dioxane solution and that of silica composite indicate that MEH-PPV was successfully incorporated in inorganic glass, retaining its π-conjugated structure. Since Wittig reaction is often used for preparation of π-conjugated polymers, a number of π-conjugated polymer/silica composites are expected to be obtained employing the sol−gel technique.

Preparation of P3HexTh/Silica Composite. Of the many π-conjugated polymers, poly(3-alkylthiophene)s have been found to be an unusual class of polymers with good solubility, processability, environmental stability, electroactivity, and other interesting properties such as thermochromism and solvatochromism.[16−22] Therefore, their composites with silica are expected to find a wide range of potential applications. Since poly(alkylthiophene)s are neutral organic polymers which do not have any functionality that interacts with silica, we intended to introduce hydroxy functionalitiy on the alkyl side chain. Our idea is to introduce a polar functional group on poly(3-hexylthiophene) (P3HexTh). The functionalized monomer **14** was prepared in two steps using 6-chlorohexyl 2-tetrahydropyranyl ether (**11**) and 3-bromothiophene (**12**) as starting materials according to Scheme 6. The hydroxy group was masked as the 2-tetrahydropyranyl ether (THP group). The THP group, like other acetals and ketals, is inert to nucleophilic reagent and is unchanged under organometallic reactions. Holdcroft and co-workers reported preparations and polymerizations of thiophenes containing a 2-tetrahydropyranyl group.[23−25] Copolymerization of **14** with 2-bromo-3-hexylthiophene (**15**) was carried out to obtain copolymer **16** (Scheme 7). To know the effect of hydroxyl group on the compatibility with silica, copolymers with two different composition were prepared. Figure 4 shows a ^{1}H NMR spectrum of the copolymer **16**. The protons in the 4-position of the thiophene ring mainly appeared at 6.96 ppm, which denotes the head-to-tail structure. The peak at 0.9 ppm is due to CH_3 protons of hexyl group. The peaks at 4.6 and 3.8−3.3 ppm are assigned as CH and OCH_2 protons, respectively. The composition of the resulting copolymers was determined by ^{1}H NMR through the peak area ratio between the signals coming from the CH_3 protons from **15** (at 0.9 ppm) and the ones belonging to the OCH_2 protons from **14** (at 3.8−3.3 ppm). The results are summarized in Table 3. The copolymer compositions were in good agreement with the monomer feed ratios. The molar fractions of THP-functionalized thiophene in **16a** and **16b** were determined to be 0.11 and 0.22, respectively. The THP group was then removed by acid treatment in THF (Scheme 7). The reaction mixture was poured into methanol to obtain the desired copolymer **17** in quantitative yield. The ^{1}H NMR of the product is shown in Figure 5. The protons due to THP group disappeared, indicating complete conversion of **16** to **17**. The signal at 3.6 ppm can be assigned to the OCH_2 protons of 6-hydroxyhexyl group. Polymers **17a** and **17b** were with metallic lustra and soluble in THF and chloroform to give an orange solution.

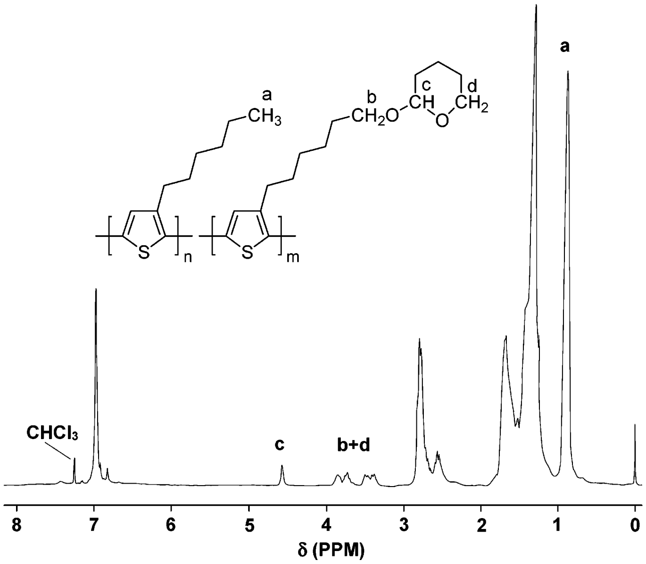
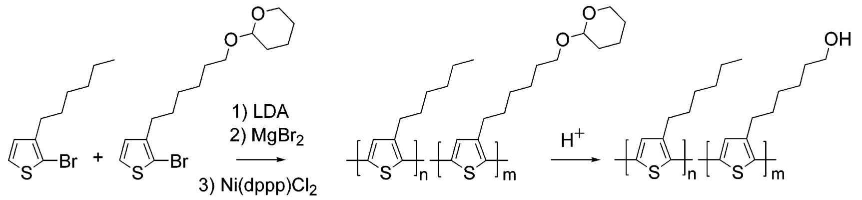


Figure 4. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) spectrum of **16b**.

The results of the sol−gel reaction of TEOS in the presence of P3HexTh, **17a**, or **17b** are summarized in Table 4. Photographs of the representative composites are shown in Figure 6. The sample using P3HexTh without hydroxy functionality showed phase separation resulting from the aggregation of P3HexTh in the silica matrix because there is no interaction between organic polymer and silica (runs 1−3). On the other hand,

Scheme 7



15 **14** **16** **17**

Table 3. Copolymerizations[a] of 14 and 15

sample	monomer feed			yield (%)	M_n[b]	copolym comp[c] *n*:*m*
	15 (mmol)	**14** (mmol)	**14** (mol %)			
16a	5.9	0.65	10	35	6000	89:11
16b	5.1	1.3	20	39	9200	78:22

[a] Conditions: diisopropylamine, 6.5 mmol; 1.6 N BuLi, 6.5 mmol; $MgBr_2 \cdot Et_2O$, 6.5 mmol; Ni(dppp)Cl_2, 0.006 mmol; THF, 30 mL; temp, rt; time, 48 h. [b] Determined by GPC. [c] Determined by ^1H NMR.

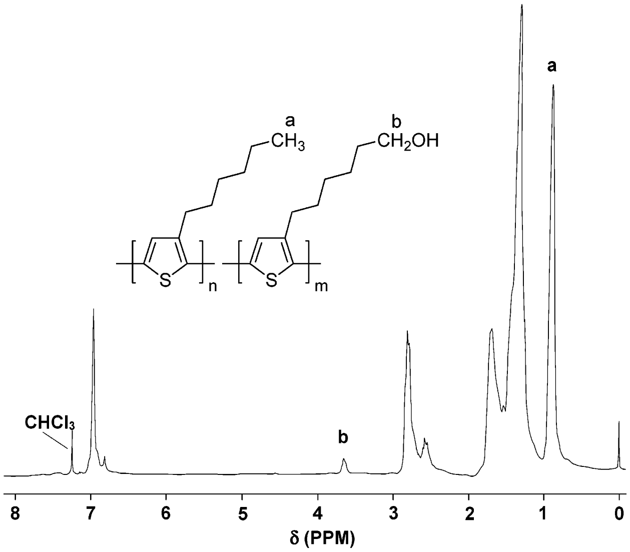


Figure 5. ^1H NMR (270 MHz, $CDCl_3$, 25 °C) spectrum of **17b**.

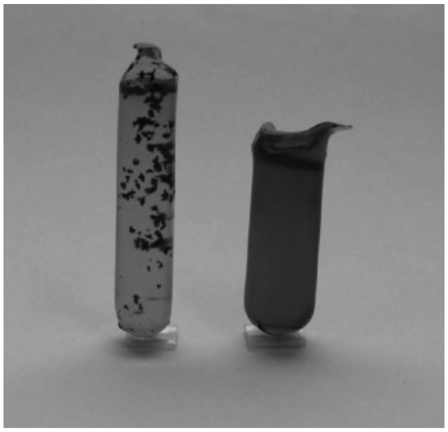


Figure 6. Photographs of silica composites obtained from run 2 (left) and obtained from run 5 (right).

Table 4. Preparations[a] of P3HexTh/Silica, 17a/Silica, and 17b/Silica Composites

run	polymer (mg)	TEOS (mL)	THF (mL)	appearance
1	P3HexTh (0.01)	4	6	phase separated
2	P3HexTh (0.05)	4	6	phase separated
3	P3HexTh (1.0)	4	6	phase separated
4	**17a** (0.01)	4	6	transparent
5	**17a** (0.05)	4	6	transparent
6	**17a** (0.1)	4	6	phase separated
7	**17b** (0.1)	4	6	transparent
8	**17b** (2.0)	4	6	transparent
9	**17b** (5.0)	4	6	phase separated

[a] 1 M HCl, 1 mL; DMSO, 1 mL.

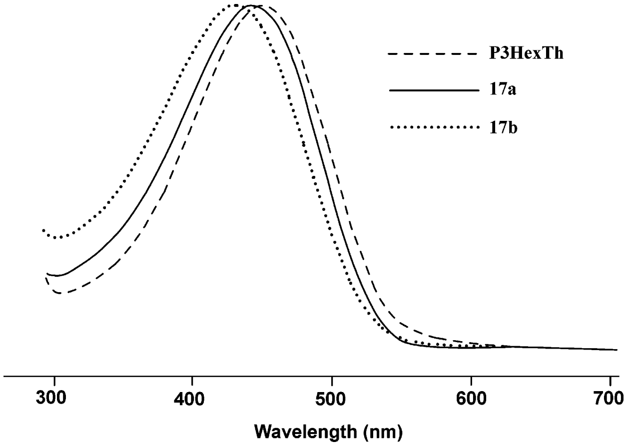


Figure 7. UV−vis spectra of P3HexTh (dashed line), **17a** (solid line), and **17b** (dotted line) in THF solution.

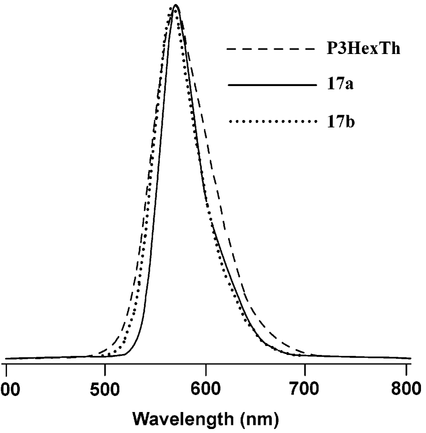


Figure 8. Photoluminescence spectra of P3HexTh (dashed line), **17a** (solid line), and **17b** (dotted line) in THF solution.

introduction of the hydroxy group was effective for homogeneous composite formation (runs 4, 5, 7, 8). Further, polymer **17b** was more compatible with silica than **17a**, indicating that hydrogen bonding between hydroxy and silanol groups played an important role in increasing the compatibility between P3HexTh and silica.

Optical Property of P3HexTh/Silica Composite. Figure 7 shows the solution UV−vis absorption spectra of P3HexTh, **17a**, and **17b**. The maximum absorption wavelengths of **17a** (445 nm) and **17b** (430 nm) were slightly blue-shifted compared to that of P3HexTh (460 nm). The reason for the blue shift of **17a** and **17b** was probably due to the small change of π-conjugated structure by the steric interaction between terminal hydroxy groups. Figure 8 shows solution photoluminescence spectra of P3HexTh, **17a**, and **17b**. No significant effect of hydroxy group was observed. These spectra showed the emission maxima at almost the same wavelength (570 nm). Figure 9 shows the photoluminescence spectra of **17a**/silica and **17b**/silica composites together with that of P3HexTh in THF solution. The emission peak of **17a**/silica composite occurred at around 570 nm, which is similar to that of P3HexTh in THF solution. This means the backbone structure of polymer **17a** in the silica matrix is essentially the same to that of P3HexTh in the solution state. The spectrum of **17a**/

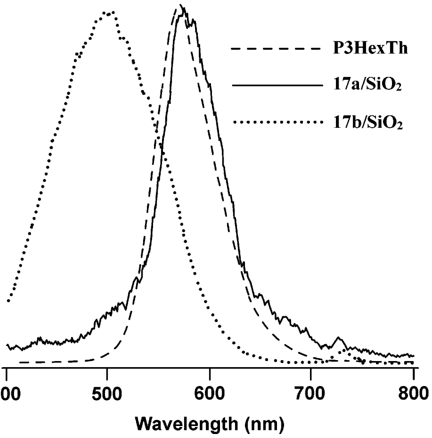


Figure 9. Photoluminescence spectra of **17a**/silica composite (solid line), **17b**/silica composite (dotted line), and P3HexTh in THF solution.

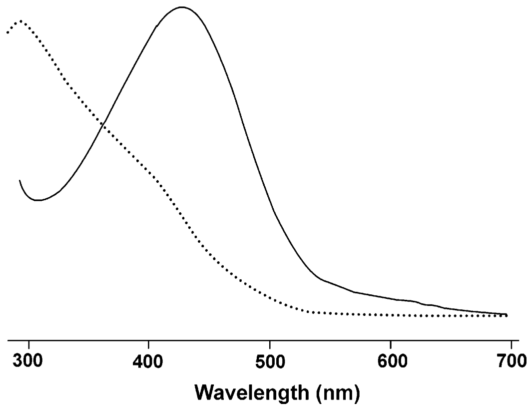
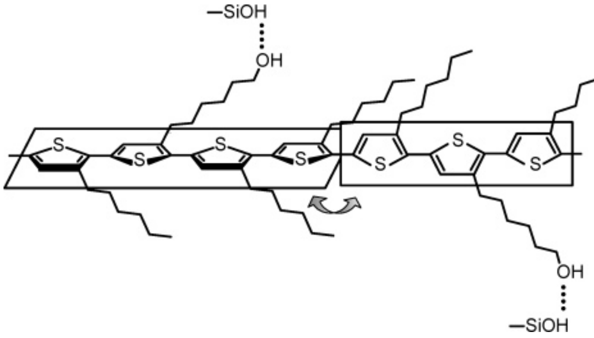


Figure 10. UV−vis spectra of **17b**/silica composite (dotted line) and its pregel solution (solid line).

silica composite is broader than that of **17a** in solution state (Figure 8, solid line), suggesting intermolecular hydrogen bonding between hydroxy group and silica. On the other hand, **17b**/silica composite showed a drastic decrease of emission wavelength compared to that of P3HexTh. The reason for this large blue shift can be explained by the decrease of π-conjugation length. The decrease of π-conjugation length was further confirmed by the change of UV−vis absorption spectrum during the sol−gel process. Figure 10 shows the UV−vis absorption spectra of **17b**/silica composite and its pregel solution. The maximum absorption wavelength shifted from 430 to 296 nm after gelation, indicating the twisting of the polythiophene segment through the interaction between hydroxy and silanol groups in the silica matrix (Scheme 8).

Scheme 8



In conclusion, we have shown molecular designs for π-conjugated polymers that form homogeneous composites with silica using the sol−gel reaction. Introduction of phousponium salt moiety at the chain end of MEH-PPV improved the compatibility with silica. MEH-PPV was successfully immobilized in silica matrix retaining its optical properties. In the case of P3HexTh, 10% introduction of hydroxy functionality onto the side chain was sufficient for homogeneous composite formation without destroying its π-conjugated structure. The introduction of too much hydroxy group on P3HexTh caused the decrease of conjugation length due to the stronger interaction between hydroxy group and silica. These findings will open the way to the preparation of a wide variety of π-conjugated polymer/silica composites as light-emitting, nonlinear optical, and conductive materials.

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