

Synthesis and Characterization of Blue Light-Emitting Polymers Containing Phenylenevinylene Units

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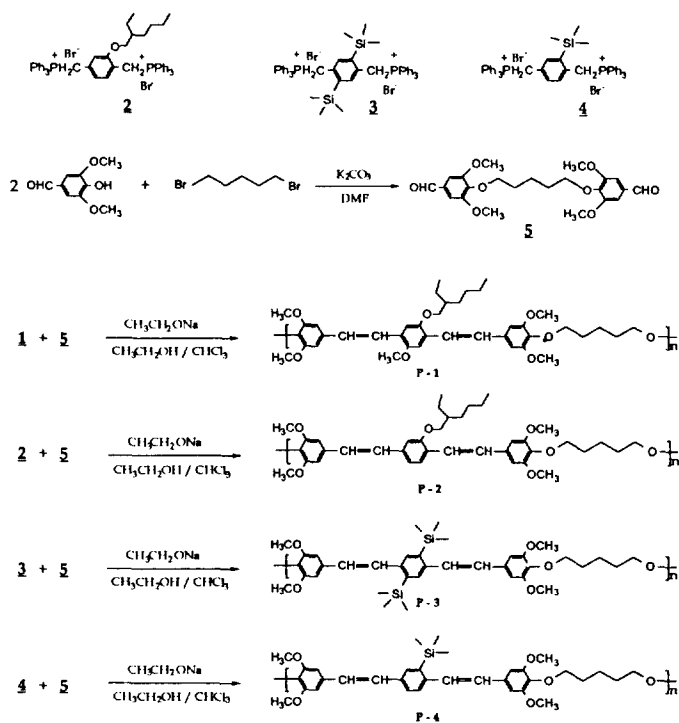
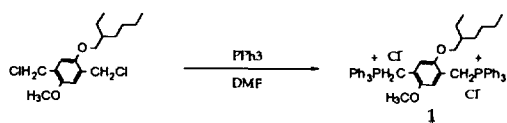
A series of new polymers containing phenylenevinylene (PV) units were synthesized by Wittig polycondensation⁷ reaction and properties of the synthesized polymers were characterized by FT-IR and UV-visible spectroscopy, and their light-emitting properties were studied. All of the synthesized polymers were soluble in organic solvents and showed good film quality. The absorption maxima and band edges of the polymers were moved to shorter wavelength region by reducing the electron donating alkoxy groups incorporated in phenylenevinylene unit. The photo-induced emission spectra were obtained and all of the polymers revealed their emission in blue region. The observed emission maxima of the polymers were ranged from 480-495 nm.

Introduction

The interests in organic light-emitting polymers have been increased in recent years since Burroughes *et al.* firstly reported a green light-emitting diode (LED) using poly(*p*-phenylenevinylene) (PPV) as the emitting layer.¹ Up to now, inorganic light-emitting diodes and lasers have mainly progressed, but they still have some problems in the fabrication process of the diodes, and especially in the realization of green or blue light-emitting devices.² On the other hand, organic polymer LEDs have many advantages in the development of a large-area visible light-emitting display.²⁻⁴ Among them, the most attractive advantage of the polymer LED is the versatile color tuning of light-emission particularly in the blue region through the molecular design of polymeric materials.⁵ The blue light emitting properties of poly(alkylfluorene)⁶ and fully conjugated poly(*p*-phenylene) (PPP)^{7,8} were reported. But the blue light emission of PPV and its derivatives could not be obtained, even with partially eliminated ones of PPV derivatives, because of the random distribution of the conjugation length in PPV. Recently, Yang *et al.* reported the synthesis and the blue light-emitting properties of PPV derivatives with well defined conjugation length.^{9,10} This suggests that the emission in blue region can be obtained by regulating the conjugation length of the conjugated polymers.

In this article, we report the synthesis and characterization of a series of blue light-emitting polymers, where we controlled the number of alkoxy group incorporated in phenylenevinylene unit of the polymers. Flexible long alkoxy side chains and trimethylsilyl groups were also introduced in phenylene ring as substituents to improve the solubility of the polymers. The synthetic schemes and polymer structures are shown below.

Synthetic Scheme



Experimental

Synthesis of the monomers

2-Ethylhexyloxy-5-methoxy-1,4-xylenebis(triphenylphosphonium chloride) (1). A solution of 5.0 g (15.0 mmol) of 2-ethylhexyloxy-5-methoxy-1,4-bis(chloromethyl)benzene¹¹ and 8.7 g (33.0 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 hours. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer **1**, was obtained as a white powder. The product yield was 11.2 g (87%): ¹H NMR (DMSO-d₆) δ 7.87-7.54 (m, 30H), 6.75 (s, 1H), 6.53 (s, 1H), 5.06 (d, 2H), 4.95 (d, 2H), 2.94 (s, 2H), 2.79 (s, 3H), 1.30-0.95 (m, 9H), 0.84 (t, 3H), 0.71 (t, 3H); mp 201-202 °C (dec). Elem anal. Calcd: C, 74.19; H, 6.53. Found: C, 70.32; H, 6.45; IR (KBr) 2905, 1431, 1220, 1113, 748, 691 cm⁻¹.

2-Ethylhexyloxy-5-methoxy-1,4-xylenebis(trimethylsilylphosphonium chloride) (3).

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nium bromide) (2). A solution of 5.0 g (13.0 mmol) of 2-ethylhexyloxy-1,4-bis(bromomethyl)benzene¹² and 7.4 g (28.0 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 hours. The product yield was 10.0 g (85%): ¹H NMR (DMSO-d₆) δ 7.91-7.51 (m, 30H), 6.87 (d, 1H), 6.50 (d, 1H), 6.44 (s, 1H), 5.23 (d, 2H), 4.90 (d, 2H), 2.85 (s, 2H), 1.23-0.95 (m, 9H), 0.86 (t, 3H), 0.69 (t, 3H); mp 230-232 °C (dec). Elem anal. Calcd: C, 68.11; H, 5.89. Found: C, 65.62; H, 5.78; IR (KBr) 2903, 1435, 1268, 1110, 748, 690 cm⁻¹.

2,5-Bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) (3). A solution of 7.4 g (7.4 mmol) of 2,5-bis(trimethylsilyl)-1,4-bis(bromomethyl)benzene¹³ and 4.3 g (16.3 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 hours. The product yield was 6.1 g (89%): ¹H NMR (DMSO-d₆) δ 7.94-7.55 (m, 30H), 7.05 (s, 2H), 5.01 (d, 4H), -0.31 (s, 18H); mp 299-300 °C (dec). Elem anal. Calcd: C, 64.35; H, 5.79. Found: C, 63.02; H, 6.04; IR (KBr) 2850, 1435, 1261, 1108, 840, 690 cm⁻¹.

2-Trimethylsilyl-1,4-xylenebis(triphenylphosphonium bromide) (4). A solution of 3.0 g (9.0 mmol) of 2-trimethylsilyl-1,4-bis(bromomethyl)benzene¹⁴ and 5.2 g (19.8 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 hours. The product yield was 6.2 g (80%): ¹H NMR (DMSO-d₆) δ 7.91-7.49 (m, 30H), 7.25 (s, 1H), 6.78 (d, 1H), 6.65 (d, 1H), 5.80 (d, 2H), 5.01 (d, 2H), -0.15 (s, 9H); mp 233-235 °C (dec). Elem anal. Calcd: C, 65.56; H, 5.35. Found: C, 61.85; H, 5.33; IR (KBr) 2855, 1420, 1250, 1109, 996, 843 cm⁻¹.

1,5-Bis(4-formyl-2,6-dimethoxyphenoxy)pentane (5).

A solution of 10.0 g (54.9 mmol) of 4-hydroxy-3,5-benzaldehyde, 6.3 g (28.0 mmol) of 1,5-dibromopentane and 4.1 g (30.0 mmol) of potassium carbonate in 100 mL of DMF was stirred and refluxed for 24 hours. The resulting mixture was poured into cold water. The precipitate was collected and dried in vacuum desiccator. A pure white solid product was obtained by recrystallizing the precipitate from ethanol. The product yield was 7.1 g (60%): ¹H NMR (200 MHz, CDCl₃) δ 9.82 (s, 2H), 7.08 (s, 4H), 4.05 (t, 4H), 3.86 (s, 12H), 1.83-1.71 (m, 4H), 1.61 (m, 2H); mp 77-79 °C. Elem anal. Calcd: C, 63.88; H, 6.53. Found: C, 62.18; H, 6.00; IR (KBr) 2950, 2738, 1693, 1588, 1424, 1130 cm⁻¹ (Figure 1(a)).

Polymerization. A solution of 0.3 g of sodium ethoxide in 10 mL of anhydrous ethanol was added to a stirred solution of 0.5 g (1.6 mmol) of the dialdehyde monomer, **5**, and 1.4 g (1.6 mmol) of 2-ethylhexyloxy-5-methoxy-1,4-xylenebis(triphenylphosphonium chloride), **1**, in 10 mL of ethanol and 10 mL of chloroform at room temperature. Soon, a yellow-green precipitate was formed and the mixture was stirred for 10 hours after the addition. The reaction mixture was extracted with dichloromethane and water. After drying and removing the solvent, crude polymer product was obtained. Then, the product was redissolved in dichloromethane and precipitated in methanol. After filtration and vacuum drying, a yellow-green colored poly[1,5-pentanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-ethenylene-(2-ethylhexyloxy-5-methoxy-1,4-phenylene)-1,2-ethenylene-(3,5-dimethoxy-1,4-phenylene)], **P-1**, was obtained. Poly[1,5-pentanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-ethenylene-(2-ethylhexyloxy-1,4-phenylene)-1,2-ethenylene-(3,5-dimethoxy-1,4-phenylene)] (**P-2**), poly[1,5-pentanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,

Table 1. Molecular weights and polydispersity indices of the synthesized polymers

Polymer	\bar{M}_n	\bar{M}_w	P.D.
P-1	7100	15000	2.1
P-2	4800	12000	2.5
P-3	2700	7200	2.7
P-4	3300	5800	1.8

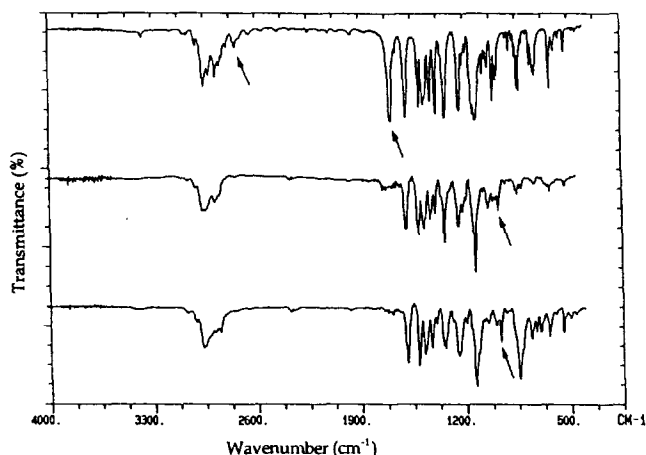


Figure 1. FT-IR spectra of (a) dialdehyde monomer, **5**, and the polymer films of (b) **P-1** and (c) **P-3**.

2-ethenylene-(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-(3,5-dimethoxy-1,4-phenylene)] (**P-3**), and poly [1,5-pentanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-ethenylene-(2-trimethylsilyl-1,4-phenylene)-1,2-ethenylene-(3,5-dimethoxy-1,4-phenylene)] (**P-4**) were synthesized by similar synthetic method with that of **P-1**.

Characterization

Melting points were determined using a Electrothermal Model 1307 digital analyzer. ¹H NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were recorded on a Bomem Michelson series FT-IR spectrophotometer and UV-visible spectra were obtained with a Shimadzu UV-3100S. Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology. The photoluminescence spectra were recorded on a Perkin Elmer LS-50 fluorometer at room temperature utilizing a lock-in amplifier system with chopping frequency of 150 Hz and an Xenon lamp as an excitation light source. The excitation wavelength was 330 nm.

Results and Discussion

All of the synthesized polymers are soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran and cyclohexanone, etc., and show the good film quality. GPC measurements of these polymers with polystyrene as the calibration standard showed the weight average molecular weight between 5,000-15,000 with polydispersity index of 2-3. The detailed molecular weights and polydispersity indices are listed in Table 1.

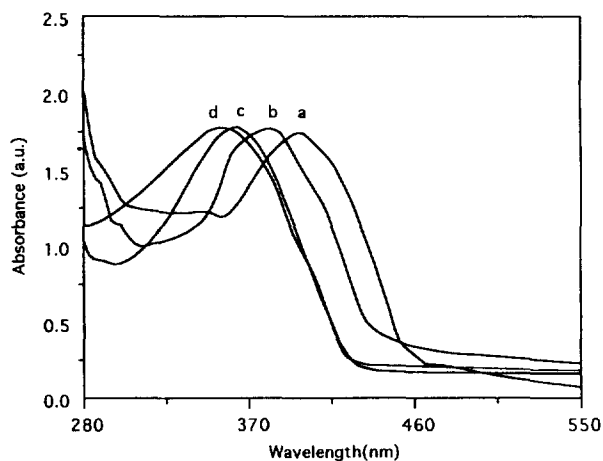


Figure 2. UV-visible spectra of the polymer films of (a) P-1, (b) P-2, (c) P-3 and (d) P-4.

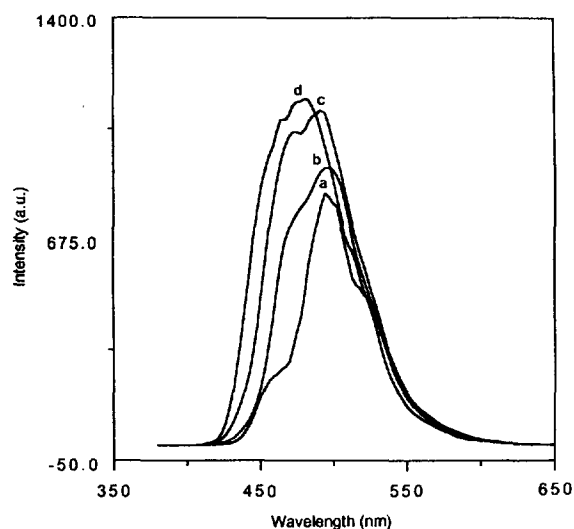


Figure 3. Photoluminescence spectra of the polymer films of (a) P-1, (b) P-2, (c) P-3 and (d) P-4.

Figure 1 shows the FT-IR spectra of the dialdehyde monomer 5 and the polymer films of the P-1 and P-3. In Figure 1 a), the dialdehyde monomer 5 shows the strong absorption peak of the aldehyde carbonyl group at 1701 cm^{-1} and also the characteristic absorption peak of aldehyde at 2730 cm^{-1} , but in Figure 1 b) and c), these absorption peaks drastically decreased after polymerization, at the same time weak but sharp absorption peak at 960 cm^{-1} appears which corresponds to the out-of-plane bending mode of the trans-vinylene group, suggesting that the generated double bonds are mainly trans configuration.

Figure 2 shows UV-visible spectra of the polymers. P-1 polymer shows absorption maximum and band edge at 398 nm and 457 nm, respectively. P-2, P-3 and P-4 show the absorption maxima and band edges at more blue region than those of P-1. These blue-shifted absorption properties can be explained by the reduction of the number of electron donating alkoxy groups incorporated in phenylenevinylene unit. Figure 3 shows the photoluminescence (PL) spectra of

Table 2. Absorption maxima, band edges and emission maxima of the synthesized polymers

Polymer	λ_{max} (UV) (nm)	Band edge (nm)	λ_{max} (PL) (nm)
P-1	398	457	495
P-2	380	436	495
P-3	364	426	490
P-4	356	423	480

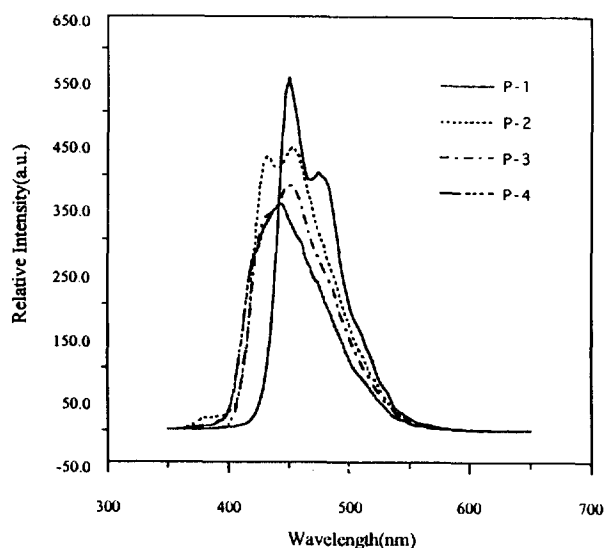


Figure 4. Photoluminescence spectra of the polymer solutions in dichloromethane.

the polymers. The observed emission maxima were ranged from 480-495 nm. All of the polymers show the emission in blue region, but the changes of the emission maxima of the polymers are not large like as those of the UV-visible spectra. P-4 shows the emission maximum at the most blue region among those of the synthesized polymers. The absorption maxima, band edges and the emission maxima of the polymers are listed in Table 2.

To investigate the relative PL intensity, the polymers were dissolved in dichloromethane with the same optical density at the excitation wavelength, 330 nm. The PL spectra of the polymers in dichloromethane solution are shown in Figure 4. The emission maxima of the polymer solutions were moved to the shorter wavelength about 40 nm than those of the pure polymer films because of the solvent effect. As the number of alkoxy group incorporated in the fluorophore increases, the PL intensity of the polymer increases, though the difference of intensity is not large.

Generally electroluminescence spectrum is known to be very similar to that of the PL spectrum,^{15,16} so we expect that all of the synthesized polymers will show their electroluminescence in blue region. Our synthesized polymers which have the good processibility and blue light-emitting properties may be good candidates for applications to the polymer LEDs. The electroluminescence and detailed luminescent properties of the polymers are in progress.

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Dehydrogenative Polymerization of New Alkylsilanes Catalyzed by $Cp_2MCl_2/Red-Al$ System (M = Ti, Hf)

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Substituted 3-phenyl-1-silabutanes, 3-chlorophenyl-1-silabutane (**1**), 3-tolyl-1-silabutane (**2**), and 3-phenoxyphenyl-1-silabutane (**3**), were prepared in 68-98% yield by reduction of the corresponding substituted 3-phenyl-1,1-dichloro-1-silabutanes with $LiAlH_4$. The dehydrogenative homopolymerization and copolymerization of the silanes were performed with $Cp_2MCl_2/Red-Al$ (M = Ti, Hf) catalyst system. The molecular weights of the resulting polymers were in the range of 600 to 1100 (*vs* polystyrene) with degree of polymerization (DP) of 5 to 8 and polydispersity index (PDI) of 1.6 to 3.8. The monomer silanes underwent the dehydrogenative polymerization with $Cp_2TiCl_2/Red-Al$ catalyst to produce somewhat higher molecular weight polysilanes compared with $Cp_2HfCl_2/Red-Al$ catalyst.

Introduction

Polysilanes with unusual optical and electronic properties have received a copious amount of attention as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.¹⁻³ The conventional synthetic method to get high molecular weight polysilanes to date has been the Wurtz coupling reaction of dichlorosilanes with sodium, which are intolerant of some functional groups and other limitation for controlling stereochemistry and molecular weight.

Harrod's recent discovery of the group 4 metallocene-catalyzed dehydrogenative polymerization made a large advance in polyorganosilane synthesis.⁴ Two mechanisms have been so far suggested: (1) the oxidative addition/reductive elimination sequences *via* the intermediacy of transition-metal silylene complexes⁴ and (2) the four-center sigma bond metathesis processes among silicon, hydrogen, and a d^0 metal

center *via* the intermediacy of transition-metal silyl and hydride complexes.⁵ The latter mechanism is strongly supported by many model reactions⁵ and thermochemical results.⁶ A major disadvantage of the metallocene-catalyzed dehydrogenative coupling method is to produce low molecular weights of polysilanes.^{4,5} Considerable efforts have been made to increase the molecular weight of the polysilanes.⁷⁻¹⁰

²⁹Si NMR technique has been useful in analyzing polysilane chain microstructure.¹¹ The structures of all polysilanes so far synthesized *via* dehydrogenative coupling method are predominantly random atactic although some diastereomeric selection was observed in the special reaction conditions.¹² To date, most of silanes which have been employed in the literature are arylsilanes. There are few reports on the dehydrogenative coupling of alkylsilanes.^{8,13} To our knowledge, there is no report to date on the dehydrogenative copolymerization of alkylsilanes.

The dehydrogenative coupling route of substituted 3-phe-