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Synthesis and characterization of poly(*p*-phenylene vinylene) polymers containing the quinoxaline group

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Summary

Novel poly (*p*-phenylenevinylene) polymers containing the quinoxaline group were prepared by the Horner-Wadsworth-Emmons reaction of the various diphosphonic acid diethyl ester with a dialdehyde monomer. The spectral properties of products so obtained were characterized by UV-visible and fluorescence spectroscopy. The UV-visible absorbance of these polymers showed absorption bands at ca. 432~440 nm, which corresponding to the π-π^* transition of the conjugated system. Their maximum fluorescence appeared at ca. 488 ~ 498 nm. The resulting polymers showed greenish blue emission in solution and an orange emission in solid state.

Introduction

The importance of π-conjugated polymers has increased due to their advantages and their wide potential applications. Fully π-conjugated polymers have good processability, and mechanical and chemical properties compared to inorganic materials. A number of such polymer systems (e.g. polythiophene, poly (*p*-phenylene) and their derivatives) had been previously investigated [1-8]. In particular, the poly (*p*-phenylene)vinylene (PPV) and its derivatives have been the most extensively studied for using in light emitting devices (LEDs), since these polymer types were demonstrated by Burroughes et al. [4]. However, relatively few studies have been performed on these polymer systems in association with n-type electrically conducting properties.

It is known that the electron deficient nitrogen containing moieties enhance the electron affinity of the polymer [9-11]. Poly quinoxalines have electron-accepting properties because they have two nitrogen atoms at the 1,4-position in the quinoxaline ring. Some reports have been published about the synthetic methods and characteristics of various polyquinoxalines. And it is known that their characteristics may be controlled by modifying substituents and their locations within the polymeric structure [12, 13].

In this study, we designed and synthesized poly (quinoxaline-2,3-diyl) derivatives, with a long chain alkyl group at the 6,7-position in the quinoxaline ring. Their optical and electrical properties were also investigated.

Experimental

General Methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 FT-NMR Spectrometer in chloroform-d_6 and chemical shifts were reported in ppm unit with tetramethylsilane as an internal standard. Infrared spectra were measured as KBr pellets on a MAGNA-IR 760 spectrometer, where the percentage of transmittance versus the wavenumber (cm^{-1}) were plotted. The Molecular weights and the molecular weight distribution of the polymers were measured by gel permeation chromatography (GPC) equipped with a Waters 717plus Autosampler, Water 515 HPLC pump, Waters 410 refractive index detector, and Water styragelOHR series (eluent: THF 35°C, flow rate: 0.3 ml/min). Polystyrene standards were used to calibrate the columns. UV-visible absorption curves were obtained in chloroform on an UNICAM 8700. Fluorescent spectra were measured on a SHIMADZU RF-5301PC spectrophotometer. Differential scanning calorimetry (DSC) was obtained using a TA Instrument 2100, under nitrogen flow at a heating rate of 10°C/min.

All chemicals were reagent grade and used without further purification.

Monomer Synthesis

2,3-Bis(bromomethyl)-6,7-bis(dodecyloxy quinoxaline) (1)

The reaction mixture of 1-bromobutane-2,3-dione (18g , 70 mmol), an equivalent amount of 1,2-bis(dodecyloxy)-4,5-diaminobenzene, and a catalytic amount of *p*-toluenesulfonic acid in methanol (50ml) was refluxed for 2hr under nitrogen atmosphere. The 1,2-bis(dodecyloxy)-4,5-diaminobenzene was prepared by the literature process [14]. After the reaction was completed, the reaction mixture was cooled to room temperature and the precipitate was filtered off. The crude product was purified with activated carbon in chlorofrom at 40 °C for 40 min. The solvent was removed and the greenish-yellow solid was obtained in 65 % yield. ^1H NMR ($CDCl_3$, ppm): δ 7.28 (s, 2H, quinoxaline), 4.87 (s, 4H, $-CH_2Br$), 4.16 (t, 4H, $-OCH_2-$), 1.92 (m, 4H, $-CH_2-$), 1.53-1.26 (m, 36H, $-CH_2-$), 0.88 (t, 6H, CH_3); IR (KBr, cm^{-1}) 1231 (ether).

[3-(Diethoxy phosphoryl methyl)-6,7-bis-dodecyloxy-quinoxalin-2-yl methyl] - phosphonic acid diethyl ester (2)

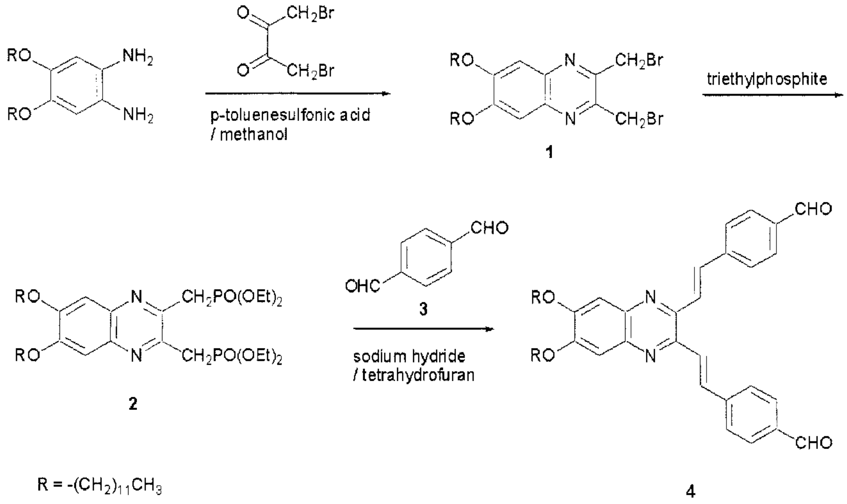
The direct phosphorylation of compound **1** gave to [3-(diethoxy-phosphoryl methyl)-6,7-bis-dodecyloxy-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester (**2**) in 91 % yield. The resulting compound was used in the next step without purification. ^1H NMR ($CDCl_3$, ppm): δ 7.27 (s, 2H, quinoxaline), 4.16-4.04 (overlapped, 12H, $-OCH_2-$, $O=P-CH_2$), 3.92 (d, 4H, $O=P-O-CH_2$), 1.92 (m, 4H, $-CH_2-$), 1.53-1.26 (m, 44H, $-CH_2-$, ethyl-CH_3), 0.88 (t, 6H, $-CH_3$); IR (KBr, cm^{-1}) 1250 (P=O).

2,3-Bis{4-(2-ethenyl)-benzaldehyde}-6,7-bisdodecyloxy quinoxaline (4)

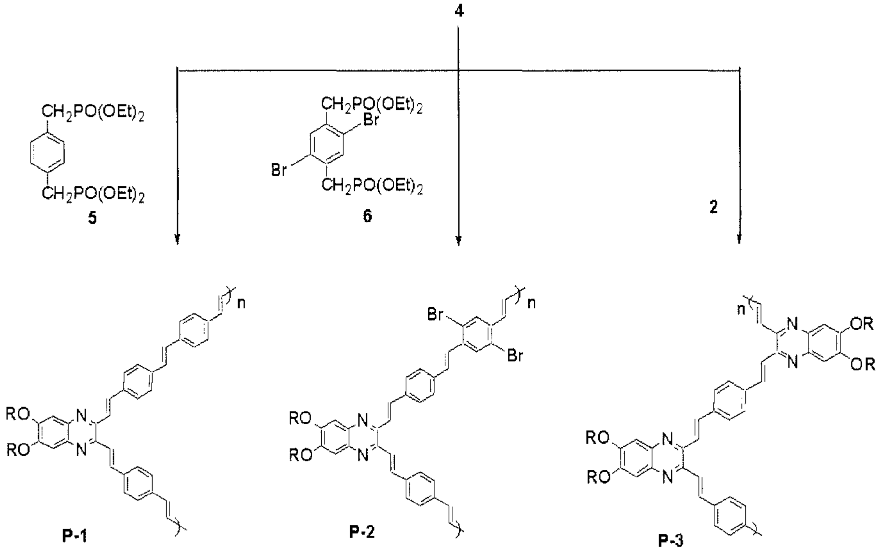
Novel quinoxaline containing monomer **4** was synthesized by the Horner-Wadsworth-Emmons (HWE) reaction. To a solution of terephthalaldehyde **3** (2.1 g, 16 mmole) in 20 ml tetrahydrofuran at 0℃ was added slowly sodium hydride (0.16 g, 7 mmole) with stirring. To the reaction mixture was added a solution of compound **2** (2.5 g, 3.2 mmole) in tetrahydrofuran (20 ml). The reaction mixture was stirred at room temperature until all of compound **3** was disappeared by TLC. After the reaction was completed, methanol was added to the reaction mixture. Filter off the precipitate and wash with methanol. The crude product was purified by column chromatography in 66% yield. The synthetic route of monomer was shown in Scheme 1. ^{1}H NMR ($CDCl_3$, ppm): δ 9.98 (s, 2H, -CHO), 7.94-7.74 (overlapped, 12H, aromatic and vinyl protons), 7.20 (s, 2H, quinoxaline), 4.14 (t, 4H, $-OCH_2-$), 1.89 (m, 4H, $-CH_2-$), 1.49-1.20 (m, 36H, $-CH_2-$), 0.82 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$, ppm): δ 191.6, 153.4, 145.4, 142.6, 139.4, 136.1, 134.6, 130.3, 127.8, 125.9, 106.8, 69.2, 31.9, 29.6(overlapping), 29.3, 28.8, 26.0, 22.7, 14.1; IR (KBr, cm^{-1}) 1697 (C=O). Elem anal. Calcd.: for $C_{50}H_{66}N_2O_4$: C, 79.11; N, 3.69; H, 8.76. Found: C, 77.54; N, 3.72; H, 8.75.

Polymerization.

A solution of monomer **4** (0.76g 1 mmol), [4-(diethoxyphosphoryl-methyl)-benzyl]-phosphonic acid diethyl ester **5** (0.38 g, 1 mmol), and sodium hydride (0.06 g, 2.3 mmol) in 10 ml dichlorobenzene was heated at 95~100℃ for 18 hr under nitrogen atmosphere. The precipitated yellow solid (polymer 1;**P-1**) was filtered and washed thoroughly with methanol, and then dried *in vacuo*. Polymer 2(**P-2**) and polymer 3(**P-3**) were carried out the same method of monomer **4** with compound **6** and **2**, respectively. The synthetic route of polymers was shown in Scheme 2. ^{1}H NMR ($CDCl_3$, ppm): δ 7.54-7.11 (br, aromatic and vinyl protons), 4.18 (br, $-OCH_2-$), 1.91 (br, $-CH_2-$), 1.29 (br, $-CH_2-$), 0.89 (br, $-CH_3$); IR (KBr, cm^{-1}) 1685-1689 (aldehyde, C=O stretching).



Scheme 1. Reaction route of monomer.



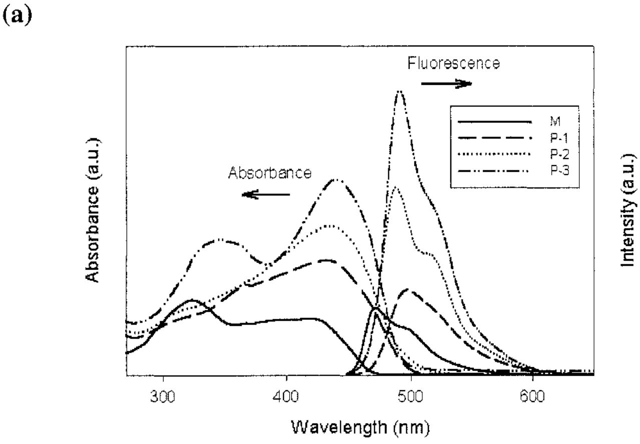
Scheme 2. Chemical structures of polymers.

Results and Discussion.

The HWE reaction of [3-(diethoxy-phosphoryl methyl)-6,7-bis-dodecyloxy-quinoxalin-2-yl methyl] -phosphonic acid diethyl ester (**2**) and terephthalaldehyde (**3**) in THF gave the quinoxaline containing monomer 2,3-bis{4-(2-ethenyl)-benzaldehyde}-6,7-bisdodecyloxy quinoxaline (**4**) in good yield (66%). Polymerization was successfully carried out by the HWE reaction of monomer **4** with compound **5**, **6** and **2**, respectively. In the ^{13}C NMR spectrum of **4**, the peak corresponding to the aldehyde was appeared at 191.6 ppm. The peaks corresponding to each carbon of the structure of the monomer were observed at appropriate chemical shifts (see Experimental section). The chemical structures of the resulting polymers were identified by ^1H NMR and FT-IR. The ^1H-NMR spectra of the monomer indicated that the benzaldehyde protons appeared as a singlet at 9.98 ppm. The terminal $-CH_3$ of the long alkyl chain appeared as a triplet at 0.83 ppm, and $-O-CH_2$ protons split as triplet at 4.16 ppm. In the case of the polymers, a broad peak was observed and the terminal benzaldehyde proton resonance was dramatically reduced. From the FT-IR spectra of the polymers, a drastic reduction of the band at 1697 cm^{-1} was observed, which corresponded to the aldehyde carbonyl stretching band of the monomer. The polymers were found to have satisfactory solubility in chlorinated hydrocarbons, THF, and benzene, but pratically insoluble in DMF, alcohols, and acetone. The polymerization results of polymers are summarized in Table 1. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the polymers were in the range 4397-9637 and 4871-18486 with a polydispersity index of 1.11-1.92. By thermogravimetric analysis (TGA), **P-1**, **P-2**, and **P-3** gradually lost 2% by weight on heating to 306, 326, and 351°C, respectively, and then showed rapid weight losses at 384, 386, and 390°C.

Table 1. Polymerization results and characterization of **P-1**, **P-2**, and **P-3**

Polymer	M_n	M_w	PDI	T_m (°C)	T_{id}(°C)	Yield(%)
P-1	9637	18486	1.92	102.6	375	23
P-2	4976	8667	1.74	103.1	362	28
P-3	4397	4871	1.11	100.8	372	25



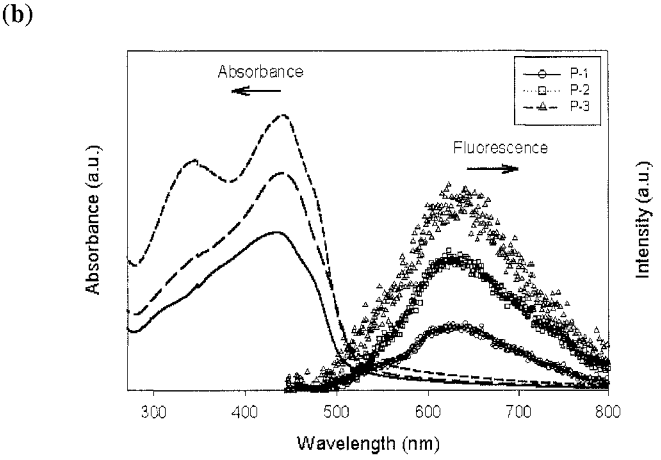


Figure 1. UV-visible and fluorescent spectra of monomer and **P-1, P-2** and **P-3** (a) in chloroform amd (b) film.

Table 2. Visible and Fluorescence Spectra of polymers

	λ_{max} (nm)		$\Delta\lambda$ [b]	F_{max} (nm) [c]		ΔF [d]	SS [e]
	$CHCl_3$	solid[a]	(nm)	$CHCl_3$	solid	(nm)	(nm)
P-1	432	438	6	498	612	114	66
P-2	436	440	4	488	614	126	52
P-3	440	440	-	492	628	136	52

[a] Spin coated thin film [b] $\Delta\lambda = \lambda_{max}$(solid) - λ_{max}(solution)
[c] Excited at absorption maximum light [d] $\Delta F = F_{max}$(solid) - F_{max}(solution) [e] Stokes' shift

The absorption and fluorescence spectra in chloroform solution and as solid thin films of polymers are summarized in Figure 1 and Table 2. The monomer showed two absorption maxima in chloroform solution (324 and 420 nm), which were attributed to the π-π^* transitions of the quinoxaline group and of the phenylene vinylene segment, respectively. The absorption maxima of polymers in chloroform solution were observed at 432-440 nm and these showed bathochromic shifts resulting from the π-π^* transitions of the conjugated polymer backbone. The absorption spectra of the polymers were similar to that of the solution state. The fluorescence maxima of polymers were observed at 488-498 nm (greenish blue) when excited at absorption maximum light. However, the fluorescence peaks of the polymer films were observed at 612-628 nm (yellow). The red shifted fluorescence maximum in the solution versus the solid state is caused by intermolecular molecular interactions and their stabilization in excited state on solid state. The ΔF value, which indicates the difference between F_{max} in the solid state and in solution state, changed from 114 nm in **P-1** to 136 nm in **P-3**. It is interesting that the polymer showed a greenish blue fluorescence in solution but red fluorescence in solid state. More detail analyses of these polymeric molecular stacking behaviors will be reported separately.

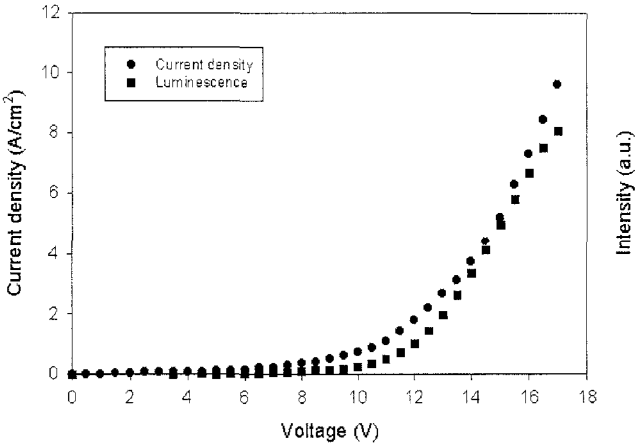


Figure 2. Current voltage characteristics of **P-1.**

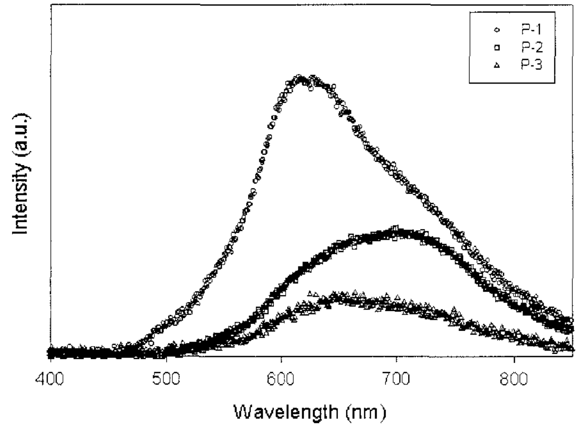


Figure 3. EL spectra of polymers.

The resulting polymers, as described above, were deposited onto indium tin oxide covered glass substrates by spin coating. Figure 2 shows the current-voltage (I-V) characteristics of **P-1.** The turn-on voltages of the polymers were found to be approximately 5, 4, and 2 V, respectively. The EL spectra were found to closely resemble the fluorescence spectrum of the polymer thin film, but a small difference was observed at the longer wavelength region (Figure 3). Thus, these polymers are expected to be useful materials for the manufacture of polymer-based light-emitting diodes (LEDs).

Conclusion

Novel poly (*p*-phenylenevinylene) polymers containing the quinoxaline moiety were successfully synthesized by the HWE reaction. The resulting polymers showed greenish blue emission in solution state and an orange emission in solid state. The turn-on voltages were determined in the range of 2-5 V from the I-V curves.

Acknowledgements.

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