

퀴녹살린을 포함한 신규 전기 발광성 고분자의 합성

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Design and Synthesis New Electroluminescent poly(*p*-phenylenevinylene) polymers containing Quinoxaline

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Introduction

Today, interest in electroluminescent(EL) diodes has been increasing since vacuum-sublimed thin-film diodes exhibited high performance. And since the discovery of electroluminescence from aluminquinone, which has uniform π -conjugated segment by Eastmann kodak,¹ lots of attentions have been concentrated on organic EL devices. However, they have disadvantage such as low mechanical intensity, thermic crystallization. In order to complement a this point it makes with polymer. Polymeric material are expected to be suitable for EL devices because they have good mechanical intensity, high thermal stability, good processability. And the first of the polymer EL base on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,² and then a number of different polymers have been synthesized and extended efforts have been made to obtain high performance devices from polymeric material.^{3,4} It introduces the substitution which is suitable as it increases the effect of the EL.^{3,5}

Few of pyrazine derivatives have been known as dye chromophores, so we used quinoxaline containing pyrazine in making monomer as new synthetic reagent. Pyrazine has two nitrogen atoms at 1,4-position to replace of carbon atoms in benzene ring, and is expected to many functionalities, and reactivities compared with their benzene analogues. Based on design concept for charge transport and emissive materials which has been established in sublimed-dye system and polymer-dispersed dye system, we started our study to extend our material design concept towards polymers with EL chromophores in skeletal chains. In this paper, we deal with the synthesis and optical properties of quinoxaline-containing monomer and polymers in main chain.

Experimental

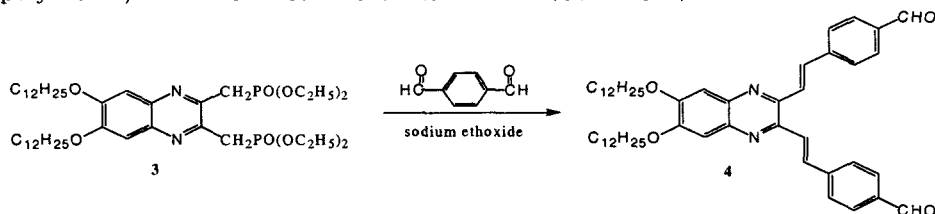
Preparation of monomer The monomer was prepared by starting alkylated catechol. Alkylated catechol gave 1,2-bis(dodecyloxy)-4,5-dinitrobenzene that was reduced to 1,2-Bis(dodecyloxy)-4,5-diaminobenzen.(1)⁶

In a round bottomed flask(100mL), were placed 1 (4.0g, 8mmol), 1-Bromo-but-ane-2,3-dione(2.1g, 8mmol), p-toluenesulfonic acid(0.02g, 0.1mmol) in methanol(40 mL) under a nitrogen atmosphere. The mixture was refluxed and filtered. After the crude product was washed with charcoal in chloroform at 30~40°C, the mixture was filtered. Finally, the resulting solid product was recrystallized 2,3-Bis-bromomethyl-6,7-bis-dodecyloxy-quinoxaline(2) from methanol. 4.2g(6.1mmol) as 76% yield

In a round bottomed flask(100mL), were placed 2 (3.4g,5mmol) and triethyl phosphite(1.7g, 10mmol). The mixture was refluxed. After they were purified by silica gel column chromatography. the solvent was evaporated away. Finally, the resulting solid product was recrystallized [3-(Diethoxy-phosphorylmethyl)-6,7-bis-dodecyloxy-quinoxalin-2-ylmethyl]-phosphonic acid diethyl ester(3) 2.8(3.5mmol)g of 3 was obtained as 70% yield

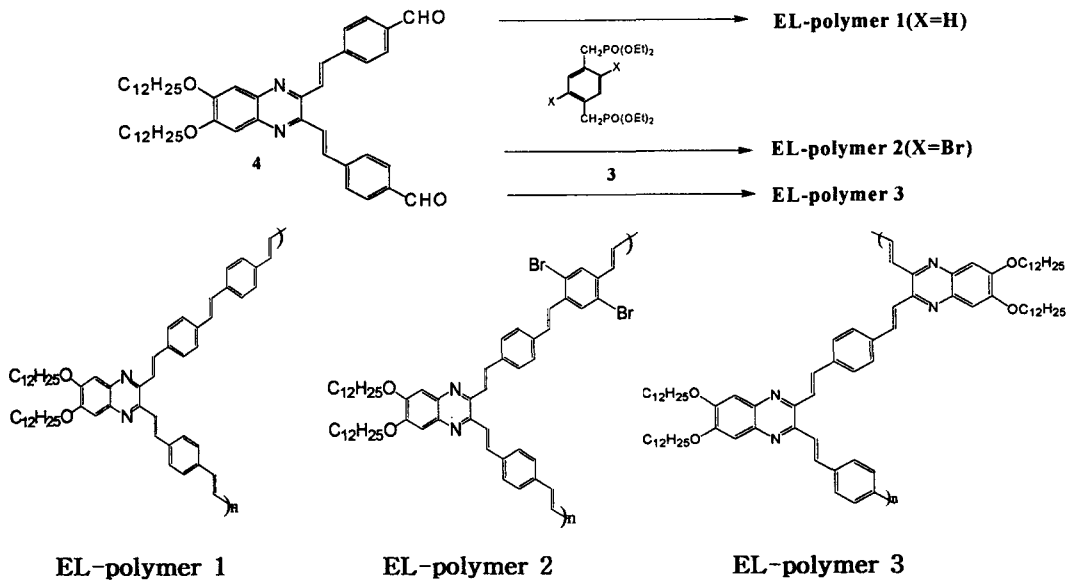
monomer, 2,3-Bis(4-(2-ethenyl)-benzealdehyde)-6,7-bisdodecyloxy quinoxalin(4) Novel quinoxalin-containing monomer was synthesized by the Wittig reaction route(Scheme 1). Place Benzene-1,4-dicarbaldehyde(2.1g,16mmole) and THF(20mL) in three-necked the flask. And add slowly, sodium hydride(0.16g, 7mmole) with stirring. When the temperature has fallen to 15°C introduce slowly, with stirring, a solution of 3(2.5g 3.2mmole) in THF(20mL), at such a rate that the temperature does not exceed 15°C. Filter the solid and wash it with water. Dry in a vacuum desiccator. 1.6g(2.1mmol) of 4 was obtained as 66% yield

polymer In a round bottomed flask(100mL) , were placed 4(0.76g 1mmol), [4-(Diethoxyphosphoryl-methyl)-benzyl]-phosphonic acid diethyl ester(0.38g, 1mmol), sodium hydride(0.06g 2.3mmol) in dichlorobenzene(10mL). Under N₂ the mixture was refluxed at 95~100°C for 18hr. The reaction mixture was filtered and washed with methanol. Finally, the resulting solid product was EL-polymer 1. And EL-polymer 2,3 were carried out same method.(Scheme 2)



Scheme 1. Synthesis of monomer by the Wittig reaction

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Scheme 2. Synthesis of EL-polymers

Table 1. Polymerization Results of Quinoxaline-Containing EL-polymers

polymers	yield(%)	M_n^a	M_w^a	PDI	$T_m(^{\circ}\text{C})$	$\lambda_{\text{max}}(\text{nm})$	$F_{\text{max}}(\text{nm})$
EL-polymer 1	23	9637	18486	1.92	102.57	433	498
EL-polymer 2	28	4976	8667	1.74	103.11	433	488
EL-polymer 3	25	4397	4871	1.11	100.75	438	492

^a M_n , M_w , and PDI of the polymers were determined by gel permeation chromatography. λ_{max} , $F_{\text{max}}(\text{nm})$ were the UV absorption spectra of the UV absorption spectra and photoluminescence spectra of the polymers in chloroform solution

Result and Discussion

The polymerization results of quinoxaline-containing poly(*p*-phenylenevinylene)-related polymers are summarized in Table 1. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the polymers, determined by gel permeation chromatography using polystyrene standards, were in the range of 4397–9637 and 4871–18486 with a polydispersity index of 1.11–1.92, respectively. The chemical structures of the resulting polymers were identified by FT-IR, ¹H NMR, and UV-visible spectrometry. Figure 1 shows the typical FT-IR spectra of the quinoxaline-containing PPV-related polymers. The comparison of the monomer FT-IR spectra to that of the polymer showed a drastic decrease of the bands at 1695 cm^{-1} , which is expected for the strong aldehyde carbonyl stretching band of the dialdehyde monomer. Figure 2 shows the ¹H NMR spectrum of the monomer and polymer 1 containing quinoxaline. As the polymerization, the aldehyde peak of the monomer present at 9.98 ppm disappeared and vinylic proton peaks appeared at 6.3 and 8.4 ppm overlapped with

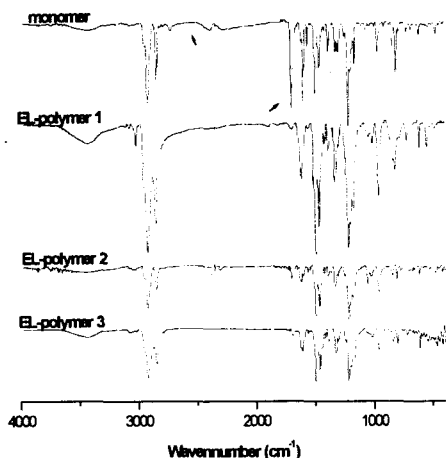


Figure 1. IR spectra of monomer and EL-polymers in KBr pellet

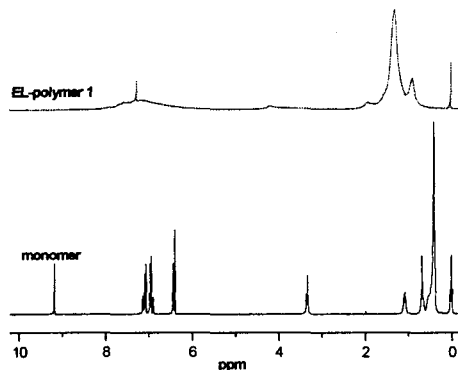


Figure 2. ¹H NMR spectra of the Quinoxaline-containing monomer and polymer

aromatic proton. Also, the peak around 4.1 ppm was assigned to the methylene protons adjacent to a hydrogen atom and the peaks of about 0.7 and 2.2 ppm were assigned to the alkyl protons. Figure 3 shows the UV absorption spectra and photoluminescence spectra of the quinoxaline-containing monomer and polymers in chloroform solution. The present quinoxaline-containing polymers show red shifts relative to monomer. Because of yielding a increasing of π -conjugation.

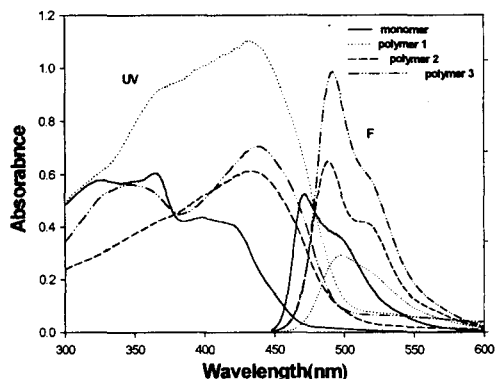


Figure 3. UV-visible spectra and Fluorescence spectra of monomer and polymers in CHCl_3

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