

Studies on the Synthesis and Optical Properties of Novel Blue Light-Emitting Polymers Containing Phosphorus and Oxadiazole Structures

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ABSTRACT: Novel phosphorus-containing polymers with high-electron-affinity oxadiazole were synthesized and characterized by thermal analysis and spectroscopy (infrared, ultraviolet–visible, photoluminescence, cyclic voltammetry) measurements. These new polymers can be used as blue electroluminescent materials and as electron-transport layers in polymer light-emitting diodes. In this study, aromatic polyethers containing electron-transporting chromophores and emission chromophores were synthesized from 2,5-bis-(4-fluoroaryl)-1,3,4-oxadiazole and 2-(6-oxido-6*H*-dibenz<c,e><1,2> oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPO-NBQ). The effects of reaction temperature and time on the formation of polyethers were investigated to obtain optimum conditions for polyether manufacturing. All the resulting polymers were thermally stable at <460 °C. The absorption peaks of these polymers were at 350–365 nm, whereas the photoluminescent peaks were at 460–481 nm. But, the intensity of polymer absorption decreased and a blue shift was observed in the photoluminescent spectra as the temperature increased. In addition, these polymers containing the electron-transporting oxadiazole indeed showed extra reduction potentials in cyclic voltammetry measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2367–2376, 2002

Key words: OLED polymer; phosphorus; oxadiazole

INTRODUCTION

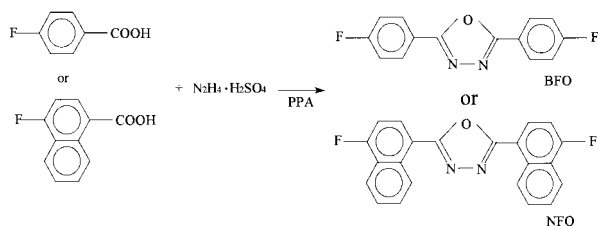
Polymers with extended π -systems are attractive for a wide range of potential applications from antielectrostatic coatings and biosensors to solar cells, photonic switching, light-emitting, and molecular electronic devices.¹ In particular, π -conjugated polymers have been considered as organic light-emitting materials for the fabrication of electroluminescent devices. The primary reason for this use is the high photoluminescent quan-

tum yield in the visible region that characterizes many of these materials, combined with the advantage of simple processability into flexible, mechanically robust films or thin layers. The conjugated polymers are favored as emitting layers for polymer-based light-emitting diodes (LEDs), particularly poly(*p*-phenylenevinylene) (PPV),² poly(*p*-phenylene) (PPP),³ and polythiophene⁴ types.

Since the first observation of electroluminescence from PPV, conjugated polymers have attracted much attention because of their potential applications in large-area display technologies. One of the attractive features of polymer electroluminescent materials is that the emission color can be controlled by altering the chemical

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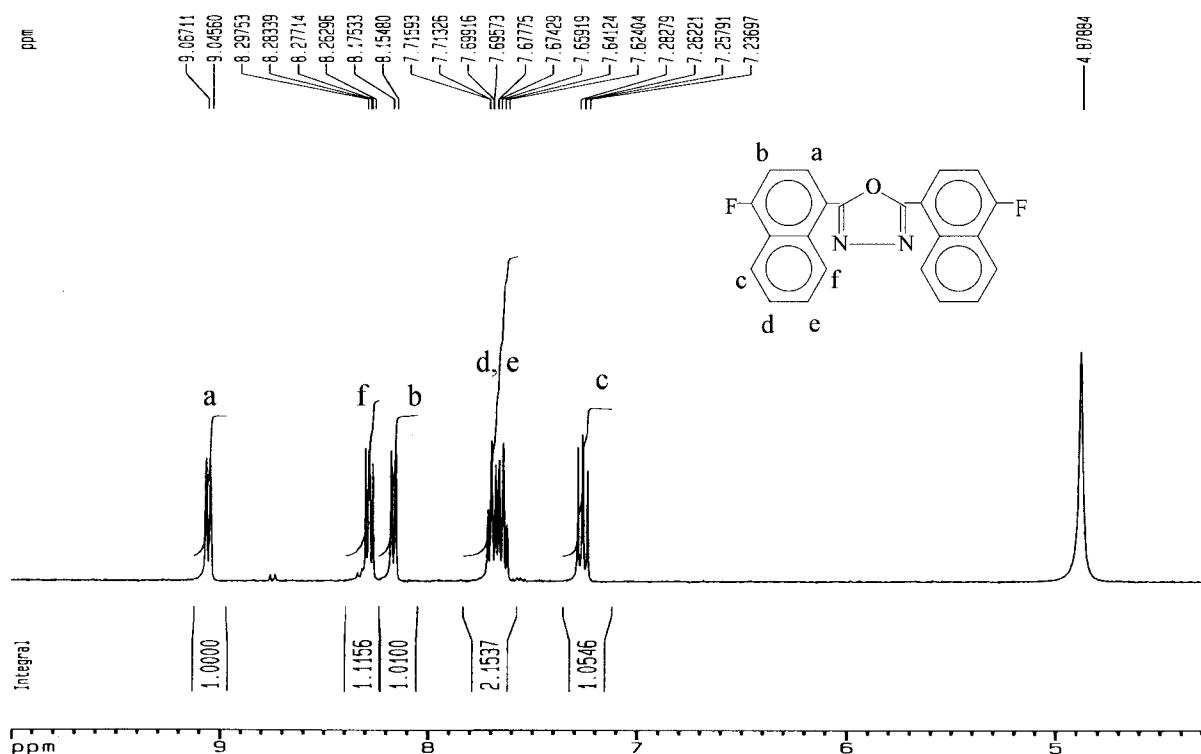


Scheme 1

structure of the polymer. PPV gives emission in the yellow-green, but the emission color can be moved toward the red by the substitution of electron-donating groups, such as alkoxy chains, at the 2- and 5- positions on the phenyl ring.⁵ Burn et al.⁶ obtained blue-green emission using a random copolymer of PPV and the methoxy-leaving group precursor to dimethoxy-PPV. So far, much attention has been paid to change the emission color of PPV containing material like either non-conjugation units introduced in the polymer backbone or groups substituted in different positions of the phenyl ring. The basic feature of a polymer LED is that the emission color can be tuned by controlling the average conjugation length of the polymer chain.

However, the ideal organic LED (OLED) does not only have tuneable emission color, but the efficiency of such electroluminescent devices needs to be further improved. Some effective methods have been developed for improving the performance by increasing the efficiency of the recombination of electrons and holes. One way is to add an electron-transport layer in between the emitting layer and cathode, allowing a balance of charge injection and transport by enhancing the transport of electrons and in some occasions blocking the transport of holes so that the recombination zone is kept away from the interface near the cathode. In recent years, both low molecular weight oxadiazole derivatives and oxadiazole-containing polymers⁷⁻⁹ have been shown to provide improved quantum efficiency and are often regarded as electron-transport layers (ETL).

In previous work,¹⁰ several novel organic light-emitting polymers containing phosphorus were synthesized, and the effect of different structures on optoelectric properties was investigated. The resulting polymer containing naphthalene rings was thermally stable below 480 °C, and its photoluminescent peak was 464 nm. Therefore, it can be adapted as a blue luminescent material in

Figure 1 ¹H NMR spectra of 2,5-bis(4-fluoronaphthyl)-1,3,4-oxadiazole (NFO).

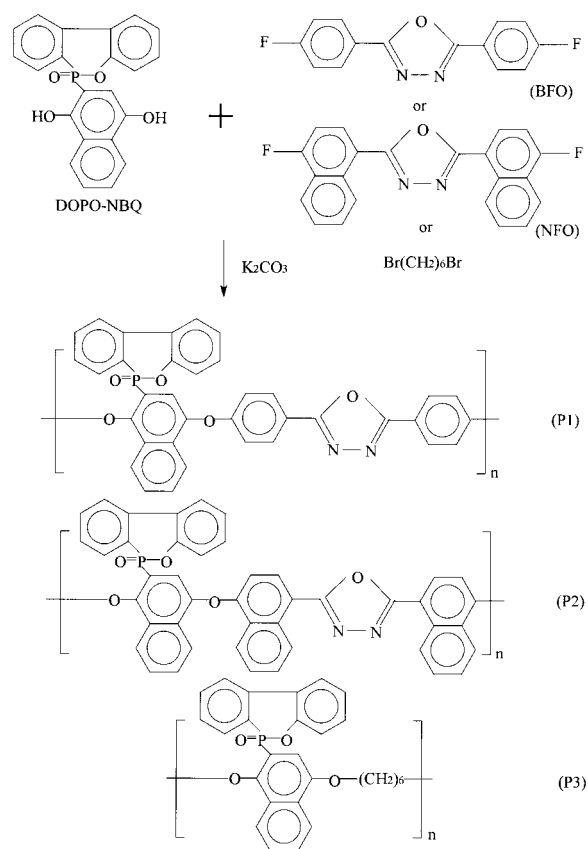
polymer LEDs. In this study, two oxadiazole-containing electron-transporting chromophores were synthesized and incorporated with 2-(6-oxido-6*H*-dibenz[*c,e*] <1,2> oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPO-NBQ). The effects of reaction temperature and time on the formation of polyethers were investigated to determine an optimum condition for polyether manufacture. Moreover, a polyether containing an aliphatic chain, instead of an electron-transport ion unit, was also synthesized for comparison. The motivation of the present work was to investigate the effects of different structures and temperature on optoelectric properties (absorption spectra, photoluminescence spectra, and cyclic voltammogram) by thermal analysis and spectroscopy.

EXPERIMENTAL

Materials and Measurement

All reagents and solvents were reagent grade or were purified by standard methods before use. 1,4-Naphthoquinone (NBQ), *o*-phenyl phenol and phosphorus trichloride (Aldrich), 1,6-dibromohexane, 4-fluorobenzoic acid, and 4-fluoro-1-naphthoic acid (Lancaster) were used as received. Ethylene glycol monoethyl ether (ethoxyethanol), *N*-methyl-2-pyrrolidone (NMP), *N*-cyclohexyl-2-pyrrolidone (CHP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), diphenyl sulfone, and methanol from Acros Company were used as solvents and purified before use.

Elemental analyses were performed with a Heraeus CHN-O-Rapid elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 5DX-B spectrophotometer. Mass spectra were recorded by a VG 70-250 S GC/MS (mass spectrometer). Melting points (T_m) of monomer were determined with a polarizing microscope (Laboratory Devices MEL-TEMP II). Intrinsic viscosity of the polymer was measured with an Ubbelohde viscometer and was calculated from the relative viscosity by the Ram Mohan Rao equation.¹¹ A thermogravimetric analyzer (DuPont Model TGA 2950) was used to measure the weight loss of polymer films during the temperature scan from 30 to 600 °C, with the heating rate of 10 °C/min in a stream of nitrogen. A differential scanning calorimeter (DuPont Model DSC 2010) was used to examine thermograms in the temperature range 30–300 °C with the heating rate of 10 °C/min. Proton nuclear magnetic resonance (¹H



Scheme 2

NMR) was performed in CD₃OD or DMSO at 50 °C. Ultraviolet–visible (UV–vis) spectra were obtained with a Perkin-Elmer Lambda 40 spectrometer. Optical characterization was performed by photoluminescence (PL) measurement, where the 325 nm line of an He–Cd laser with 20 mW power was used to excite the sample. Cyclic voltammetry (CV) was carried out in a one-compartment cell with a potentiostat/galvanostat (Model 610A from CH Instruments), with a nonaqueous electrode (0.01 M AgNO₃, 0.1 M (*n*-Bu)₄NClO₄/acetonitrile) as the reference electrode, a Pt electrode (1×3 cm) coated with a thin neutral polymer film to be tested as the working electrode, a blank platinum (Pt) strip as the counter electrode, and tetrabutylammonium perchlorate in dry acetonitrile (0.1 M) as electrolyte under a scan rate of 20 mV/s. Gel permeation chromatography (GPC) with refractive index (RI) detector and column (PL gel 5 μm MIXED-D 300×7.5 mm from England Polymer Laboratories Ltd.) was used to measure molecular weight distributions (MWDs) relative to polystyrene standards at room temperature. The calibration curve was determined with

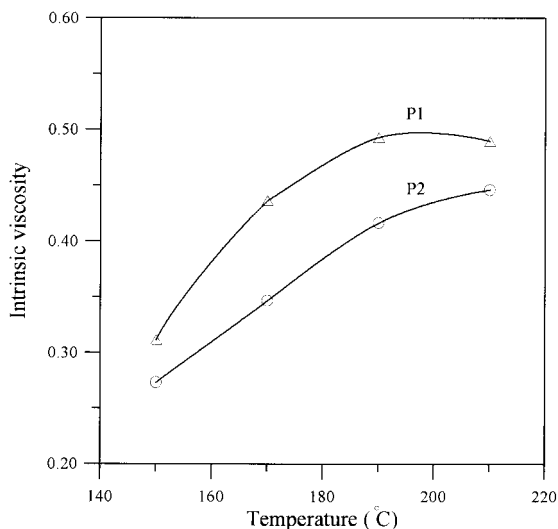


Figure 2 Effect of temperature on the polymerization of P1 (Δ) and P2 (\circ).

six MW standards from 2930 to 3.77×10^5 . The carrier solvent used was degassed NMP at the flow rate 1 mL/min.

Synthesis of 2,5-Bis(4-fluoroaryl)-1,3,4-oxadiazole (BFO and NFO)

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFO) was synthesized according to our previously published procedures¹⁰ as shown in Scheme 1. The BFO was further recrystallized from methanol and dried: yield, 76%; mp, 204–205 °C.

2,5-Bis(4-fluoronaphthyl)-1,3,4-oxadiazole (NFO) was synthesized according to our previously published procedures¹⁰ with some minor modifications. The NFO was further recrystallized from toluene and dried: yield, 70%; mp, 232–233 °C. The IR spectrum (KBr) exhibited absorption at 3066, 1675, 1598($-\text{C}=\text{N}-$), 1493, 1429, 1160, 1093, 1070, 838, 763, and 745 cm^{-1} . The shift and splitting pattern of the ^1H NMR spectrum was 7.23–7.27(dd, 2H), 7.61–7.70(m, 4H), 8.14–8.16(d, 2H), 8.25–8.29(dd, 2H), 9.03–9.05(d, 2H) (Figure 1). Anal Calcd. for $\text{C}_{22}\text{H}_{12}\text{N}_2\text{OF}_2$: C, 73.74; H, 3.35; O, 4.47; N, 7.82. Found: C, 73.78; H, 3.39; O, 4.38; N, 7.86. EIMS, m/z : 358(M^+).

Synthesis of 2-(6-Oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPO-NBQ)

DOPO-NBQ was synthesized according to our previously published procedures¹⁰ and then fur-

ther recrystallized from ethoxyethanol: yield, typically 70%; mp, 279–280 °C.

Synthesis of Organic Light-Emitting Polymer Containing Phosphorus

To a 200-mL reaction vessel, equipped with a temperature controller, overhead stirrer, and a Dean-Stark-trap, was charged 1 mmol of the respective monomers, 2.2 mmol K_2CO_3 , 15 mL of toluene, and 5 mL of NMP/CHP (v/v, 1:1). The mixture was heated to 150 °C for 3 h under intensive stirring. Then, excess toluene was removed, and the reaction mixture was isothermally heated at the final temperature for the required period of time. After cooling under nitrogen, the mixture was poured into 400 mL of acetone/methanol (v/v, 1:1) with addition of 5 mL of NMP. The mixture was further stirred at room temperature for another 24 h. The precipitate was collected, washed with distilled water, extracted with chloroform, and dried under vacuum. After drying, the polymers were obtained as gray solids. The comparison polymer containing hexamethylene chain was synthesized with DMAC instead of NMP/CHP as solvent.

RESULTS AND DISCUSSION

In this study, polymers containing electron-transporting chromophores and emission chromophores in the main chain were synthesized. The structures

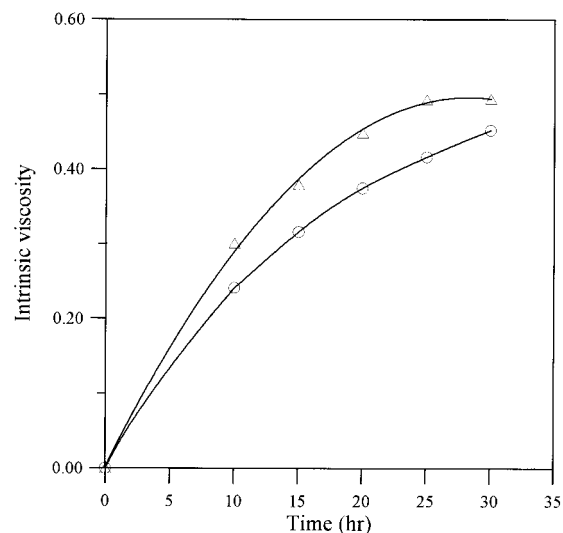


Figure 3 Time–intrinsic viscosity curves for the polymerization of P1 (Δ) and P2 (\circ) at 190 °C.

Table I Polymerization Conditions and Results for Polymers P1–P3

Item	P1	P2	P3
Reaction temperature (°C)	190	190	170
Reaction time (h)	25	30	20
Solvent	NMP/CHP	NMP/CHP	DMAc
Yield (%)	77	64	73
Calcd. ^a	C ₃₆ H ₂₁ N ₂ O ₅ P	C ₄₄ H ₂₅ N ₂ O ₅ P	C ₂₈ H ₂₅ O ₄ P
Found ^b	C _{35.8} H _{21.7} N _{1.8} O _x P	C _{44.1} H _{24.5} N _{2.3} O _x P	C _{28.2} H _{25.4} O _x P
Intrinsic viscosity (dL/g)	0.493	0.452	0.486
10 ⁻⁴ \bar{M}_w	3.4	3.2	3.4
10 ⁻⁴ \bar{M}_n	1.4	1.2	1.3
PD ^c	2.4	2.7	2.6

^a Molecular formula of repeating unit.

^b Molecular formula of repeating unit was characterized by EA measurements.

^c PD: \bar{M}_w/\bar{M}_n .

of the desired monomers from simple starting materials were confirmed by elemental analysis and mass spectrometry, and were in good agreement with the proposed structures. Polymers were synthesized according to our previously published procedures¹⁰ as shown in Scheme 2. The optical properties including absorption and luminescence of these polymers were measured by UV–vis and photoluminescent methods, respectively. CV was used to measure reduction–oxidation potentials of these polymers.

Synthesis of Organic Light-Emitting Polymer and Characterization

Polymers were synthesized according to our previously published procedures.¹⁰ The nucleophilic substitution reaction occurred by activation of the phenolic OH group with K₂CO₃ in a mixed solvent of CHP and NMP. To determine the effect of the reaction temperature on the polymerization step, 1:1 molar ratios of respective monomers were prepared, and the reaction mixture was isothermally heated at the final temperature (varied from 150 to 210 °C) for 25 h. The results are plotted in

Figure 2. These results indicate that there is an increase in intrinsic viscosity with increasing reaction temperature at the beginning; however, at a higher reaction temperature, the increase in viscosity with temperature becomes slower than in the lower temperature region. This result may be explained as follows: initially, the increase in temperature at the beginning of reaction overcame the obstacle of activation energy and resulted in the increase in the reaction rate. However, at higher temperature, side reactions may be more dominant and lead to the slower increase in viscosity. Another interesting phenomenon is observed in Figure 2; that is, NFO (containing naphthalene ring) is more thermally stable than BFO (containing benzene ring), so the polymerization for P2 can be conducted at higher temperature and obtain higher viscosity. The relationship between viscosity and isothermal (190 °C) reaction time for P1 and P2 syntheses is shown in Figure 3. The relative rates of P1 and P2 can be obtained from the initial rates in Figure 3 and approximated as P1 > P2. The reason for the difference in polymerization rates may be attributed to the fact that the steric hindrance of the

Table II Solubilities of Polymers^a

Sample	DMSO	DMAc	NMP	Pyridine	CHCl ₃	THF	Toluene
E _T (30) ^b	45.1	43.7	42.2	40.5	39.1	37.4	33.9
P1	--	+-	++	+-	--	--	--
P2	--	+-	++	--	--	--	--
P3	--	+-	++	++	+-	+-	--

^a (++) Soluble at room temperature; (+-) partially soluble on heating; (--) insoluble.

^b The polar parameter of solvent: E_T (kcal/mol) = hc ν N_A.

Table III Thermal Properties of Polymers

Polymer	T_g (°C) ^a	T_m (°C) ^a	T_d (°C) ^b
P1	262	—	505
P2	278	—	544
P3	126	212	461

^a Determined by DSC at a heating rate of 10°C/min.

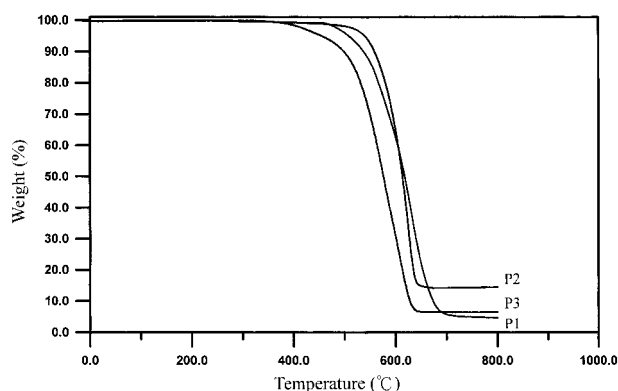
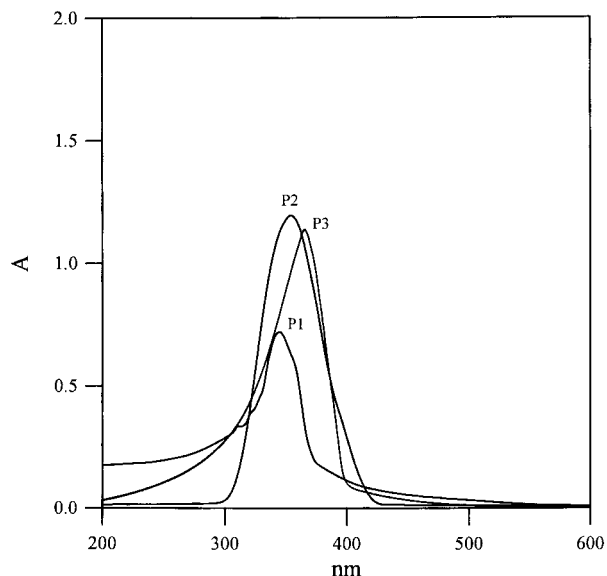
^b Temperature at which 5% weight loss was recorded by TGA at heating rate of 10°C/min.

benzene ring (BFO) is less than that of the naphthalene ring (NFO).

It may be concluded that the polymerization reaction has its own optimum operation for each polymer synthesized. The following section compares the resultant polyethers under a fixed reaction condition of 25 h (P1) or 30 h (P2) and 190 °C. This study also synthesized P3 which contains six-methylene groups in the main chain. The comparison of P3 with P1 and P2 that contain the electron-transporting chromophore will reveal the effect of the electronic affinities of these polymers. The reaction conditions and results are listed in Table I. The MWs are in the order of 10^4 (relative to the MW standards of polystyrene), which is sufficiently high to be considered as a polymer. The solubilities of polymers in various solvents are listed in Table II. Because of the introduction of aliphatic long chain segments into the polymer, P3 exhibited excellent solubility toward the test solvents. Polymer thin films of good quality could be obtained by spin coating from the polymer solutions after filtration.

Thermal Analysis of Polymer

When the polymer LED devices operate under voltage, the temperature of the device will in-

**Figure 4** TGA thermograms of P1–P3.**Figure 5** UV-vis absorption spectra of P1–P3 in the solution state.

crease, so their thermal stability is very important. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are the most favored techniques for rapid evaluation in comparing and ranking the thermal stability of various polymers. The polymers with 1,3,4-oxadiazole ring had glass transition temperatures (T_g s) in the range 260–280 °C and no T_m peak, even after the temperature went above 330°C, as shown in

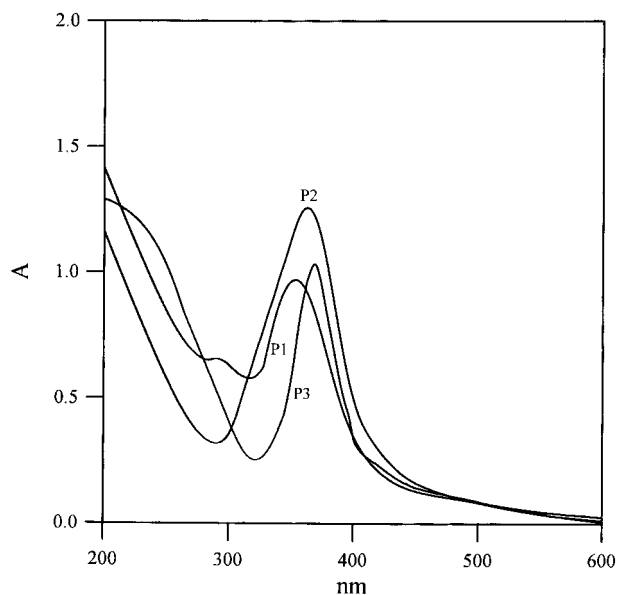
**Figure 6** UV-vis absorption spectra of P1–P3 as thin films.

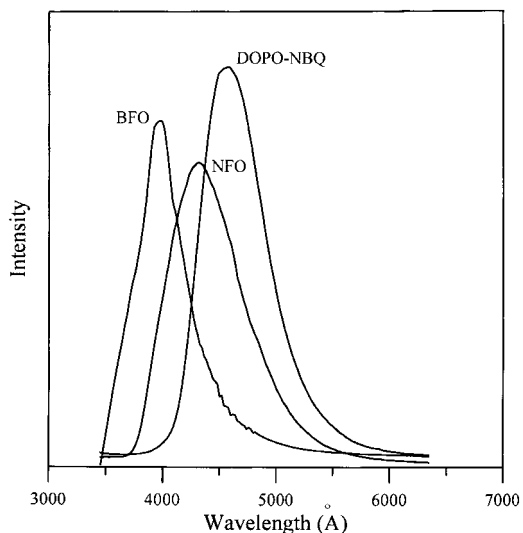
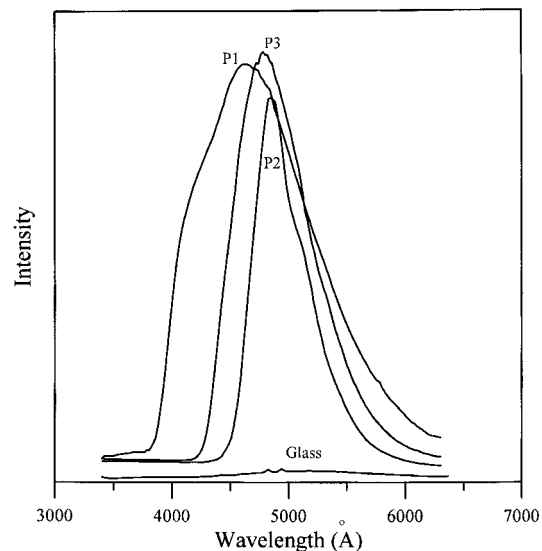
Table IV Absorption and Photoluminescent Maxima of P1–P3 in Film or Solution at Room Temperature

Polymer	UV _(solvent)	UV _(film)	PL _(film)	Stokes Shift ^a
P1	344 nm _(NMP)	350 nm	464 nm	114 nm
P2	352 nm _(NMP)	359 nm	481 nm	122 nm
P3	361 nm _(NMP)	365 nm	474 nm	109 nm

^a Stokes shift = PL_(film)/nm – UV_(film)/nm.

Table III. The T_g s of these polymers with 1,3,4-oxadiazole are much higher than that of P3 with its long aliphatic chain in the polymer. Because of the replacement of the long aliphatic chain with the rigid 1,3,4-oxadiazole groups, the rotation of polymer chains becomes difficult. Moreover, rigid naphthalene rings in the main chain of P2 obstruct the rotation of the polymer chain. Therefore, the T_g of the P2 (278 °C) is higher than those of P1 (262 °C) and P3 (126 °C). Another phenomenon observed is that the polymer containing six methylene groups crystallize easily, so P3 has a T_m at 212 °C. If the polymer crystallizes, it may separate in phases, which will reduce the device efficiency. So, P1 and P2 are the preferred material of the polymers evaluated, for OLEDs.

From the TGA results in Figure 4, it is apparent that these polymers have excellent thermal stability. The starting temperatures for degradation are all >480 °C for P1 and P2. For P3, a drastic weight decrease was observed when the

**Figure 7** Photoluminescent spectra of the monomers.**Figure 8** Photoluminescent spectra of the polymers.

temperature was close to 400 °C, whereas the drastic decrease was near 480 °C for the other polymers. The first weight loss may be due to the degradation of the aliphatic chain, and near 480 °C is the degradation of DOPO chain. As expected, polymers containing 1,3,4-oxadiazole will have higher thermal stability than that of P3 containing an aliphatic chain.

Optoelectric Properties

The emitting wavelengths of the electroluminescent polymers depend on the polymer structure. The absorption and photoluminescent spectra were measured. The UV–vis absorption spectra of polymer solution and thin film are shown in Figures 5 and 6, respectively. The peak absorption wavelengths are shown in Table IV. The data in Table IV indicate that the polymer solution has a shifted wavelength more to the blue than that of the thin film type, which may be attributed to the expansion of polymer chain in the solvent. The aggregation effects of polymers in thin film will make the energy band gap of polymers narrower than that of polymers in solution, and the wavelength will shift toward the red. This phenomenon is in agreement with previously published results.^{10, 12} The variation of the energy band gap in polymers is not only due to the variation of molecular distances but also to the polarity of solvents. Another interesting phenomenon observed is that the shift was only a few nanometers in this study, mainly because of the absence of

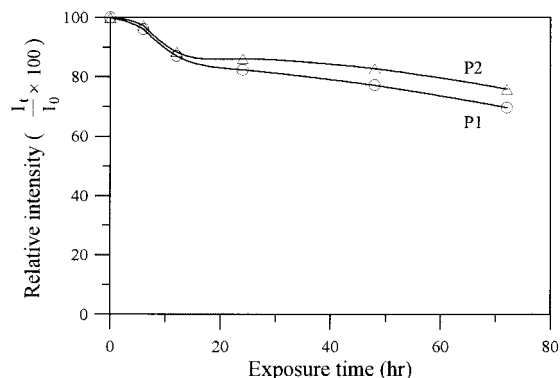


Figure 9 The relative photoluminescent intensity of P1 and P2 at different exposure times (I_0 is the initial intensity; I_t is the intensity at each exposure time).

strong donor–acceptor pairs in the emission chromophores. Although the oxygen atoms have unshared electron pairs, they are not strong donors. Another reason for the small shift is that a polymer is not as easily surrounded by solvents as a small molecule. These reasons made the absorption spectra shift less.

The photoluminescent spectra of monomers and polymers are shown in Figures 7 and 8. The peaks of photoluminescent wavelength for BFO, NFO, and DOPO-NBQ occur at 390, 442, and 454 nm, respectively (Figure 7). The photoluminescent spectra of P1 (BFO at 390 nm + DOPO-NBQ at 454 nm) will have a broad emission width

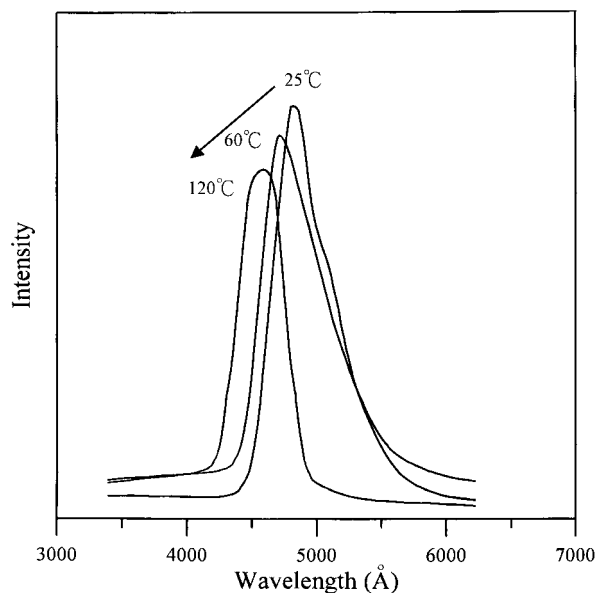


Figure 10 Photoluminescent spectra of P2 at different exposure temperatures.

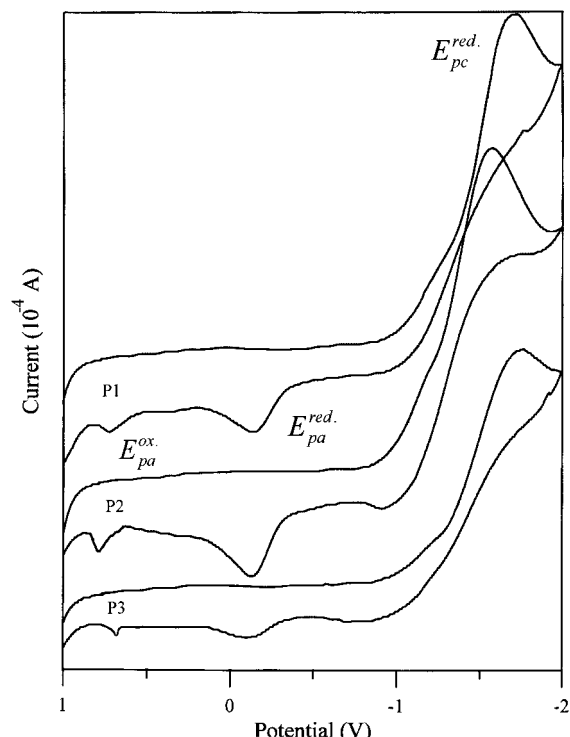


Figure 11 Cyclic voltammogram of P1–P3 in film on Pt electrode in CH_3CN solution of $(n\text{-Bu})_4\text{NClO}_4$ (0.1 M) at a scanning rate of 100 mV/s.

compared with that of P2 (NFO at 442 nm + DOPO-NBQ at 454 nm) if the emission comes from the addition of these emission chromophores. The photoluminescent wavelength of these polymers show a peak in the blue region (460–481 nm), as seen in Figure 8, so they can be used as blue emitting materials in OLEDs. The peak wavelengths are shown in Table IV, where the Stokes shift is the difference between photoluminescence and UV–vis absorption peaks. If the Stokes shift is too small, the emittance and absorption spectra will overlap more and then the emitting light will be self-absorbed and the luminescent efficiency will decrease in the devices. Because of the big Stokes shift of P2, it is the best of the polymers evaluated in this study for OLEDs.

The relationship between photoluminescent intensities and exposure times for different polymers is shown in Figure 9. Exposure times were measured only after a temperature in the vacuum oven of 120 °C had been attained. These polymers have good thermal stability as indicated by the maintenance of >82% relative photoluminescent intensity for P1 and P2 after 48 h. The relative photoluminescent intensity of P2 decreased after

Table V Electrochemical Data for P1–P3 Obtained by Cyclic Voltammetry^a

Polymer	Oxidation (V) ^b		Reduction (V) ^b	
	E_{pa}^{ox}	E_{pc}^{ox}	E_{pa}^{red}	E_{pc}^{red}
P1	0.743	— ^c	−0.141	−1.704
P2	0.845	—	−0.123	−1.561
P3	0.681	—	−0.102	−1.760

^a The measuring conditions are as follows: room temperature under nitrogen atmosphere; working electrode, platinum disc electrode; reference electrode, Ag/Ag⁺ (0.01 M AgNO₃, 0.1 M (*n*-Bu)₄NClO₄/acetonitrile) electrode; auxiliary electrode, platinum wire electrode; supporting electrolyte, (*n*-Bu)₄NClO₄ in acetonitrile.

^b E_{pa} is the anodic peak potential; E_{pc} is the cathodic peak potential.

^c Oxidation is irreversible under experimental conditions; therefore, potential values could not be determined.

exposure in the vacuum oven at different temperatures for 24 h, as shown in Figure 10, and a small blue shift was observed in the photoluminescent spectra as the temperature increased. The same phenomenon is observed for the P1 polymer. This result may be because the higher temperature will destroy the structure of polymer or cause a change in band gap of the polymer.^{13, 14}

CV provides a means for evaluating the electron affinity effect of the polymer with the 1,3,4-oxadiazole ring. This technique evaluates the electron affinity and reduction potential by scanning towards a negative voltage; it also evaluates the hole affinity by scanning towards a positive voltage. The CV spectra of P1, P2, and P3 are shown in Figure 11. The oxidation–reduction potentials are shown in Table V. No reduction wave was observed in the oxidation process, indicating that the oxidation is an irreversible process. Another phenomenon observed is that the cathodic peak potentials of P1 (−1.704 V) and P2 (−1.561 V) are less negative than that of P3 (−1.760 V). So, the electron affinity of P1 and P2, with their 1,3,4-oxadiazole rings, is stronger than that of P3, with its long aliphatic chain in the polymer. Because of the naphthalene ring, P2 is more stable than P1 in conjugation; the oxidation–reduction for P2 is easier than that for P1, as shown in Table V. The reduction potential of P2 is lower than that of P1 (the results in Figure 11 indicate P2 has higher affinity toward electrons than P1), whereas the oxidation potential of P2 is higher than P1 (the results in Figure 11 indicate P2 has less affinity toward hole than P1). Therefore, P2 is

more suitable as an electron-transporting layer than P1 in designing OLEDs.

CONCLUSIONS

Several phosphorus-containing emission chromophores were synthesized and incorporated with electron-transporting chromophores. Each polyether has its own optimum copolymerization condition. Generally, the optimum reaction conditions are 190 °C and 25 h for the DOPO-NBQ/BFO system and 190 °C and 30 h for the DOPO-NBQ/NFO system. The physical properties of polymers were successfully modified, by incorporating a 1,3,4-oxadiazole ring and using the moldability of an aromatic ether as an interval, so they generally exhibited better solubility and greater thermal stability. The photoluminescent wavelength of these polymers shows peaks in the blue region, so they can be used as blue emitting materials in OLEDs. Moreover, the relative photoluminescent intensity of polymer will decrease and a small blue shift will be observed in the photoluminescent spectra with a temperature increase. Comparison of the oxidation–reduction potential, measured by CV, indicates that P1 and P2 with 1,3,4-oxadiazole rings have less negative cathodic peak potentials than P3. It is our expectation that this result indicates that P1 and P2 should be more capable of accepting electrons than P3.

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