Synthesis and Properties of Photoluminescent Copolymer Containing 1,3,4-Oxadiazole and Carbazole Rings

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ABSTRACT: The luminescent copolymer 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole and vinylcarbazole (PMAPO–VCZ), combining hole-facilitating moiety, carbazole ring, and electron-facilitating moiety, 1,3,4-oxadiazole, as side groups, was synthesized by a radical polymerization of the olefinic monomer PMAPO and VCZ. For comparison, the homopolymer P-PMAPO was also synthesized by similar procedures. The solubility, thermal, and optical properties of the copolymers were investigated. The synthesized copolymer was soluble in common organic solvents but the homopolymer of PMAPO was dissolved only by hot THF. Thermogravimetric analysis and differential scanning calorimetry measurements showed that the copolymer and homopolymer exhibit good thermal stability up to 360 and 340°C with glass-transition temperatures higher than 105 and 65°C, respectively. The photoluminescence properties were investigated. The results showed that the copolymer emits blue and blue-green light and the emission spectra of monomer and polymers exhibit obvious solvent effect. With the increase of polarity of solvents, the fluorescence spectra distinctly change, appearing with a red shift at room temperature. The concentration-dependent emission spectra change significantly with the increase of concentration. In addition, when N,N-dimethylaniline (DMA) was gradually added to the solution of copolymers, the emission intensity of fluorescence was dramatically increased. However, when the concentration of DMA was increased beyond a certain level, the emission intensity of fluorescence gradually decreased. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2777–2783, 2004

Key words: photophysics; 1,3,4-oxadiazole; vinyl carbazole; copolymerization; charge transfer

INTRODUCTION

The use of light-emitting (LE) polymers has received a great deal of attention in academia and the optoelectronic industry because of their excellent properties and easy processability. Since the first report on the light-emitting devices (LEDs), fabricated with poly(*p*-phenylene vinylene), by the Cambridge group in 1990,[1] intensive research has been directed to synthesize, characterize, and fabricate new polymers.[2]

Low LE efficiency in some LEDs is attributed mainly to an imbalance in the transportation rates of holes and electrons in the LE layer.[3,4] To balance the transport rates and improve the device performance of polymeric LEDs, one method is to produce multilayer devices that possess hole-transporting and electron-injecting layers. Another advanced method is synthesis of new polymers containing both electron- and hole-transporting moieties to achieve efficient device performance.[5,6]

The 1,3,4-oxadiazole (OXD) unit is known to be an electron-deficient group and is efficient in promoting electron injection.[7] Poly(*N*-vinylcarbazole) (PVCZ) is characterized by good film-forming properties and has been used as an excellent hole-transport material.[8] Thus it is desirable to design and synthesize some polymers that combine the efficient hole-transport property of PVCZ unit and the high electron-injection behavior of the 1,3,4-oxadiazole unit into a single material.

In this study, a novel copolymer bearing hole-facilitating carbazole and electron-facilitating 1,3,4-oxadiazole pendants was synthesized. The results of investigation on the photophysical processes of the copolymer 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole–vinylcarbazole (PMAPO–VCZ) and the homopolymer of 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole (P-PMAPO) are reported. The solvent- and concentration-dependent photoluminescence (PL) of PMAPO–VCZ and P-PMAPO were also examined.

EXPERIMENTAL

Materials and instruments

The reagents and chemicals for preparation of monomers and polymers were used as received unless noted otherwise. Cyclohexane, benzene, THF, chloroform, acetonitrile, and N,N-dimethylaniline (DMA) were all purchased from the Beijing Chemical Plant, Beijing, China.
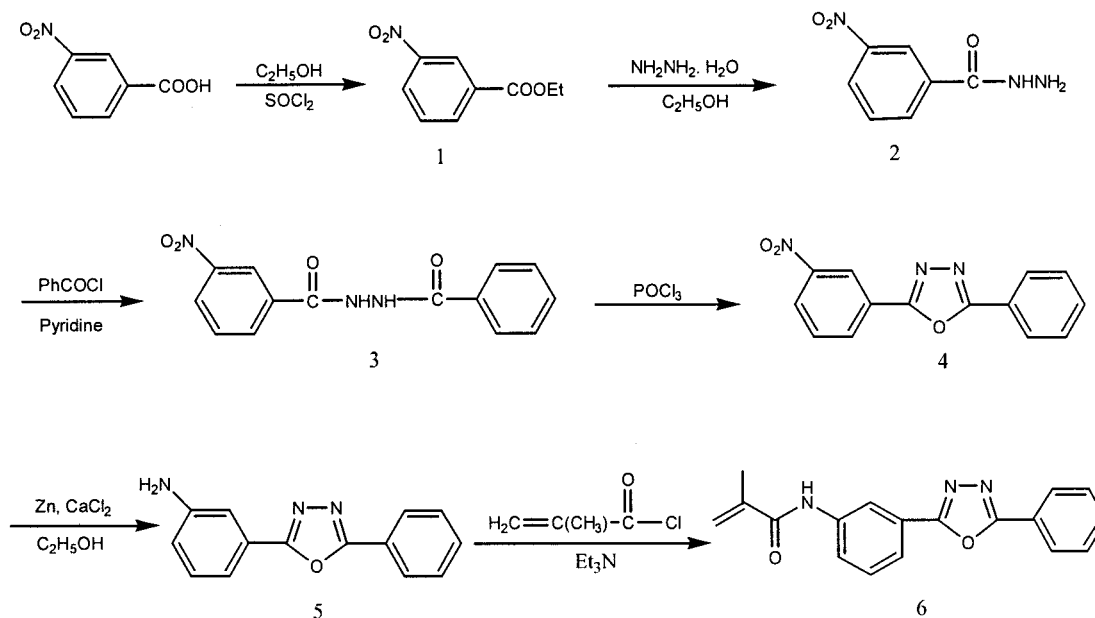
Scheme 1

analytical-grade reagents and treated according to previously established standard methods, which were all applied to measurement of the light-emitting properties.

Melting points were determined with a Sanyo Gallenkamp MPD350 melting-point apparatus and were uncorrected. NMR spectra were measured on a Bruker ARX300 spectrometer (Bruker Instruments, Rheinstetten, Germany) in chloroform-*d* solvent with tetramethylsilane as an internal standard. FTIR spectra were obtained on a PE-1700 IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Elemental analyses were performed on a Vazio elemental analyzer. The thermal properties were measured on a thermogravimeter (DT-40 TGA; Shimadzu, Kyoto, Japan) and a differential scanning calorimeter (DSC-220CU; Seiko Instruments, Tokyo, Japan). The molecular weights of the polymers were determined by a Walter 201 gel permeation chromatograph (GPC) with THF as an eluent and polystyrene as a standard. PL properties were measured on a Shimadzu RF-540 spectrofluorophotometer. Both excitation and emission bands were set at 10 nm under experimental conditions. All experiments were carried out at 25°C. For fluorescence spectra, the excitation wavelengths were 325 and 310 nm for PMAPO–VCZ and P-PMAPO, respectively. UV–vis absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer.

Synthesis of monomers (Scheme 1)

2-Phenyl-5-[3'-(methacrylamido)phenyl]-1,3,4-oxadiazole (PMAPO) monomer

Ethyl 3-nitrobenzoate (compound **1**) and 3-nitrobenzoyl hydrazine (compound **2**), shown in Scheme 1,

were prepared according to a previously reported synthetic method.[9−11] The yield of **1** was 90.6%, m.p. 42°C; the yield of **2** was 88.4%, m.p. 147°C.

N-Benzoyl-N'-(3-nitrobenzoyl)-hydrazine (compound 3)[10]. Benzoyl chloride (25 mL, 0.21 mol) was added to a solution of compound **2** (30 g, 1.17 mol) in anhydrous pyridine (150 mL) and the mixture was refluxed for 3 h. After pyridine was removed the mixture was poured into ice water, to obtain a precipitated product. The pure product, *N*-benzoyl-*N'*-(3-nitrobenzoyl)-hydrazine (compound **3**), was obtained in a 71.8% yield (33.9 g) by recrystallization from anhydrous ethanol, m.p. 219°C.

^{1}H–NMR (DMSO–d_6): δ (in ppm) 7.52 (m, 3H), 7.90 (m, 3H), 8.40 (q, 2H), 8.73 (s, 1H), 10.65 (s, 1H), 10.93 (s, 1H). IR (KBr pellet, cm^{-1}): 3225 (N—H), 1640 (C=O), 1530 (NO$_2$, as), 1350 (NO$_2$, s).

2-Phenyl-5-(3'-nitrobenzoyl)-1,3,4-oxadiazole (compound 4). Compound **3** (33.9 g 0.12 mol) in phosphorous oxychloride (POCl$_3$, 400 mL, 0.4 mol) was refluxed for 7.5 h under nitrogen. After the excess of POCl$_3$ was removed the mixture was poured into ice water and filtered. The product was then recrystallized from ethanol to give 2-phenyl-5-(3'-nitrobenzyl)-1,3,4-oxadiazole (**4**) in a 49% yield (15.6 g), m.p. 153°C.

^{1}H-NMR (CDCl$_3$): δ (in ppm) 7.60 (d, 3H), 7.78 (t, 1H), 8.19 (m, 2H), 8.52 (d, 1H), 8.54 (d, 1H), 8.96 (s, 1H). IR (KBr pellet, cm^{-1}): 1605 (C=N), 1520 (NO$_2$, as), 1350 (NO$_2$, s).

2-Phenyl-5-(3'-aminophenyl)-1,3,4-oxadiazole (compound 5)[11]. A solution of CaCl$_2$ (8 g) in water (100 mL) and compound **4** (15.6 g, 0.058 mol) were added to ethyl alcohol (600 mL). Zn powder was then added to the mixture with stirring and refluxing for 11 h. After filtering off the solid (Zn powder) and removing ethyl
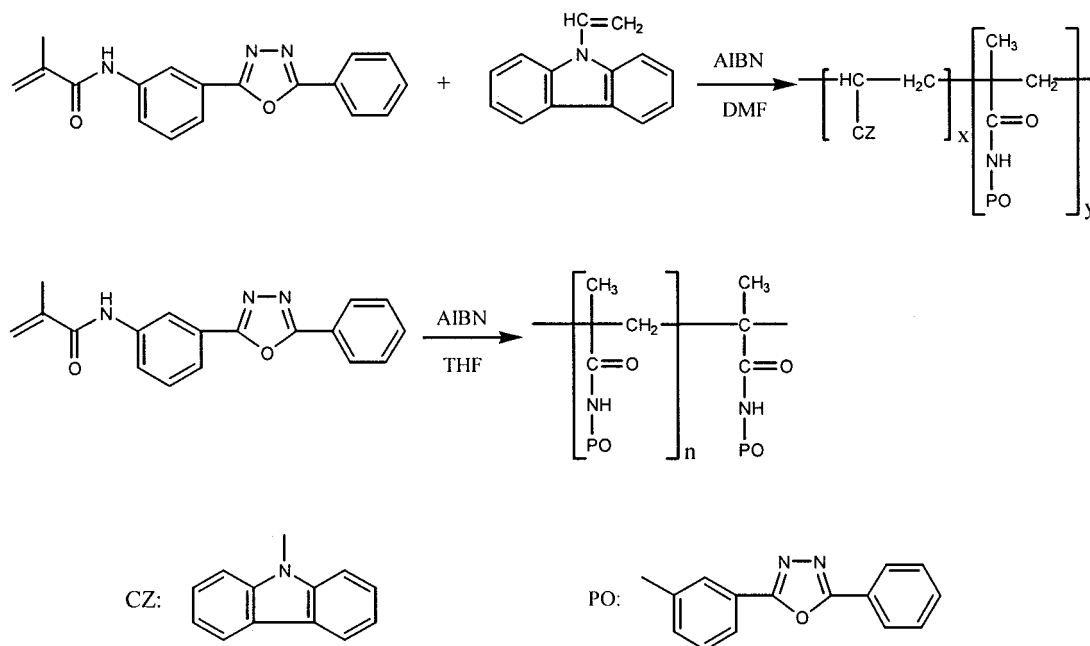
Scheme 2

alcohol from the filtrate, the solid crude product was obtained by pouring the remaining liquid into water and separating by filtration. The pure product, 2-phenyl-5-(3′-aminophenyl)-1,3,4-oxadiazole (**5**), was obtained in a 58.7% yield (8.1 g) by recrystallization from anhydrous ethanol, m.p. 176°C.

^{1}H-NMR (DMS0–d_6): δ (in ppm) 5.52 (s, 2H), 6.78 (s, 1H), 7.22–7.31 (m, 3H), 7.63 (d, 3H), 8.06 (t, 2H). IR (KBr pellet, cm^{-1}): 3450 (N—H, as), 3200 (N—H, s), 1605 (C=N).

2-Phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole (compound 6). Compound **5** (6.5 g, 27 mmol) and anhydrous pyridine were dissolved in 200 mL THF. Methacryloyl chloride (6.5 mL, 65 mmol) was then added with stirring at room temperature. The mixture was continuously stirred at room temperature for 2 h and then filtered to remove the pyridine hydrochloride. The filtrate was distilled by rotary evaporator to remove the THF solvent. The crude product was purified by recrystallization from ethanol to obtain a light yellow powder of compound **6** in a 53.8% yield, m.p. 172°C.

^{1}H-NMR (CDCl$_3$): δ (in ppm) 2.11 (s, 3H), 8.53 (s, 1H), 5.87 (s, 1H), 7.55 (m, 5H) 7.90 (t, 2H), 8.14 (t, 2H), 8.30 (s, 1H). IR (KBr pellet, cm^{-1}): 3280 (N—H), 1655 (C=O), 1620 (C=C), 1610 (C=N), 875 (H$_2$C=C<). ANAL. calcd for C$_{18}$H$_{15}$N$_3$O$_2$: C, 70.82%; H, 4.92%; N, 13.77%. Found: C, 70.53%; H, 5.09%; N, 13.68%.

9-Vinylcarbazole (VCZ) monomer

9-Vinylcarbazole (VCZ) (compound **7**) was prepared according to previously described procedures.[12]

## Synthesis of polymers (Scheme 2)

Copolymer PMAPO–VCZ

The copolymer 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole–vinylcarbazole (PMAPO–VCZ) was synthesized by copolymerization of PMAPO and VCZ. First, PMAPO (compound **6**) (0.3 g, 0.98mmol) and VCZ (compound **7**) (0.19 g, 0.98 mmol) were dissolved in THF (6 mL), followed by sufficient degassing by nitrogen gas. 2,2-Azobisisobutyronitrile (AIBN; 5 mg, 0.03 mmol) was then added. The resulting mixture was agitated for 20 h at 26°C and then poured into methanol (200 mL) with stirring to precipitate the copolymer. Reprecipitation was performed three times and the precipitated copolymer was filtered and dried in vacuum to give the white polymer PMAPO–VCZ in a 47% yield (0.36 g).

^{1}H-NMR (CDCl$_3$): δ (in ppm) 1.1 (s, 3H), 2.4 (d, 4H), 4.5 (m, 1H), 6.4–7.8 (m, 17H, aromatic), 8.0 (s, 1H). IR (KBr pellet, cm^{-1}): 3425 (N—H), 3100 (aromatic and heterocyclic C—H), 2900 (–CH$_3$, H$_2$C<), 1677 (C=0), 1520 (—$\overset{\text{O}}{\underset{\text{C}}{\|}}$—N), 1330 (aromatic C=N). The following peaks disappeared: 1620 (C=C), 875 (H$_2$C=C<).

Homopolymer P-PMAPO

In a similar manner, the homopolymer poly-(2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole) (P-PMAPO) was synthesized in a 90% yield from PMAPO.

^{1}H-NMR (CDCl$_3$): δ (in ppm) 1.1 (s, 3H), 2.5 (s, 2H), 6.9 (m, 5H), 7.5 (m, 2H) 7.8 (m, 2H), 8.0 (s, 1H). IR (KBr pellet,
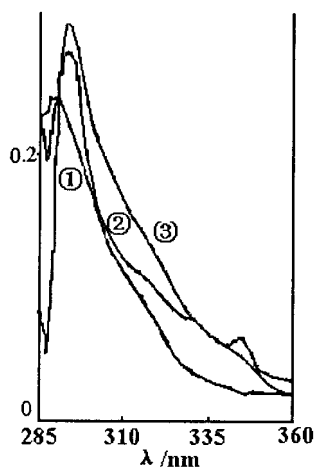
Figure 1 Absorption spectra in THF: ① PMAPO, ② P-PMAPO, ③ PMAPO–VCZ.

cm^{-1}): 3400 (N—H), 3100 (aromatic C—H), 2950 (–CH_3, $H_2C<$), 1684 (C=O), 1520 (—$\overset{\overset{O}{\parallel}}{C}$—N), 1330 (aromatic C—N). The following peaks disappeared: 1620 (C=C), 875 (H_2C=C<).

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesized monomer and polymers were characterized by ^{1}H-NMR and IR spectroscopy. The ^{1}H-NMR spectrum of monomer PMAPO shows a chemical shift of the H_2C=C< unit at δ 5.8 and 5.5 ppm. In comparison, the polymers show no features at δ 5.8 and 5.5 ppm. The IR spectra of monomer PMAPO shows sharp absorption peaks at 1620 and 875 cm^{-1} that correspond to the C=C and H_2C=C<, respectively. In the IR spectrum of synthesized polymers the IR peaks at 1620 and 875 cm^{-1} disappeared completely. The results indicate that the copolymer PMAPO–VCZ and homopolymer P-PMAPO were formed.

The copolymer PMAPO–VCZ exhibited good solubility in a range of organic solvents, including THF, 1,2-dichloroethane acetone, and chloroform, for example. The higher solubility of PMAPO–VCZ might be attributable to the 1,3,4-oxadiazole and carbazole side groups. The solubility of homopolymer P-PMAPO is low compared with that of the copolymer. It is soluble only in hot THF. The lower solubility of P-PMAPO might be attributable to the orderly stacked structure of benzene and oxadiazole rings of 2,5-diphenyl-1,3,4-oxadiazole side groups. The weight-average molecular weights (M_w) for P-PMAPO and PMAPO–VCZ, measured by GPC, were 6×10^5 and 2.1×10^4, respectively.

The thermal properties of the polymers were examined by DSC and TGA analysis. The copolymer and

homopolymer exhibited glass-transition temperatures higher than 105 and 65°C, respectively. Moreover, the copolymer and homopolymer exhibited good thermal stability, given that the weight loss was less than 5% on heating to 360 and 340°C, respectively.

Absorbance and photoluminescence properties

The UV–vis absorption spectra of the monomer PMAPO (compound **6**) and polymers PMAPO–VCZ and P-PMAPO, in THF (1×10^{-5} M), were measured (Fig. 1). The absorption spectra of monomer PMAPO and homopolymer P-PMAPO are similar in shape, with a maximum around 285–305 nm, but the absorption spectra of copolymer PMAPO–VCZ are quite different. PMAPO–VCZ shows an absorption peak about 345 nm. The additional peak at 345 nm of PMAPO–VCZ is attributed to the carbazole unit in the copolymer side chain.

The photoluminescence (PL) spectra of the monomer and polymers were measured with excitation wavelengths corresponding to their absorption maximum wavelengths. The emission peaks appeared in the nearly blue region.

Solvent effects on photoluminescence

To gain a deeper understanding of the PL properties of polymers, the solvent effects and concentration effects on photoeluminescence of polymers were investigated. The fluorescence spectra of the dilute solutions of copolymer PMAPO–VCZ and homopolymer P-PMAPO were measured in different solvents, and all results are shown in Figures 2 and 3. The maximum emitting wavelengths λ_{max}, in different solvents, are listed in Table I.
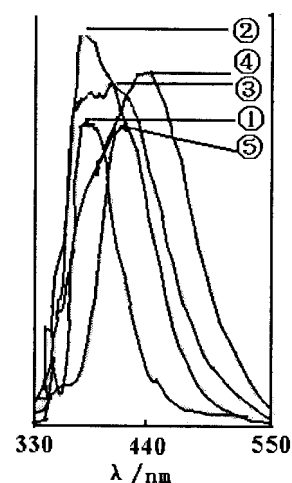
Figure 2 Fluorescence spectra of PMAPO–VCZ in different solvents: ① cyclohexane, ② benzene, ③ THF, ④ chloroform, ⑤ acetonitrile.
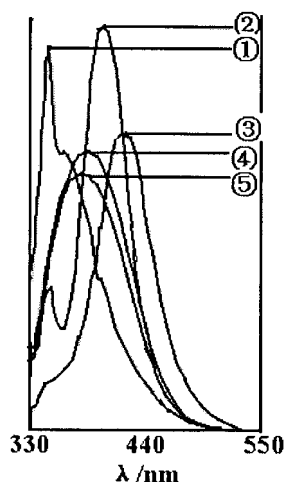
Figure 3 Fluorescence spectra of P-PMAPO in different solvents: ① cyclohexane, ② benzene, ③ THF, ④ chloroform, ⑤ acetonitrile.

It can be seen from Table I that fluorescence spectra of monomer PMAPO, copolymer PMAPO–VCZ, and homopolymer P-PMAPO distinctly change with the increase of polarity of solvents.[13] The red shift of emission peaks with the increase of polarity of solvents was observed.

The 1,3,4-oxadiazole unit (OXD) is an electron-deficient group and has substantial electron affinity, so the monomer and polymer containing the oxadiazole moiety are polar chemicals, which explains why their emission spectra exhibit an obvious solvent effect.

Generally, the red-shift phenomenon of emission spectra of chromophore occurs with increase of solvent polarity, attributed to dipole–dipole interaction of the excited state. However, from Figure 3 we can see that the aromatic solvent, benzene, and aliphatic solvents have different effects on the fluorescence of homopolymer P-PMAPO. The emission spectra of P-PMAPO in benzene are more red-shifted than those in aliphatic solvents, THF and chloroform. The results are likely attributable to the π–π interactions between the polymer chains and aromatic solvents. Both the homopolymer and aromatic solvent, benzene, have aromatic rings, and thus π–π stacking interactions may exist, except the general dipole–dipole effect. It was previously reported that the polymer chains may be more rigid in an aromatic solvent than in aliphatic solvents. Consequently, the effective conjugation systems of P-PMAPO in benzene are relatively increased.[14] Aliphatic solvents, such as THF and chloroform, provide a much different chemical environment from that of the aromatic solvents. The interactions of P-PMAPO and aliphatic solvents are mainly caused by the dipole–dipole interactions.

Quite different from the homopolymer P-PMAPO, the emission spectra of copolymer PMAPO–VCZ in

TABLE I
Maximum of Emission Spectra of Monomer (PMAPO), Copolymer (PMAPO–VCZ), and Homopolymer (P-PMAPO) in Different Solvents

Solvent	λ_{cm}^{max}		
	PMAPO	PMAPO–VCZ	P-PMAPO
Cyclohenxane	357	344	374
Benzene	364	395	380
THF	381	377	405
Chloroform	400	381	435
Acetonitrile	408	415	415

the aromatic solvent benzene are not more red-shifted than in the aliphatic solvents THF and chloroform (Fig. 2). It is easy to understand that the intramolecular actions of PMAPO–VCZ between the carbazole ring and the oxadiazole ring are more important than the π–π stacking interactions between the copolymeric chain and the aromatic solvent.

Concentration effects on PL

Figures 4 and 5 show the emission spectra of the copolymer PMAPO–VCZ and the homopolymer P-PMAPO in THF with different concentrations, respectively. The emission spectra change dramatically with different concentrations. As shown in Figure 5, the emission peak of homopolymer P-PMAPO in dilute solution is at about 395 nm. When the concentration is increased, the intensity of the emission peak is gradually decreasing and red shifts. Quite different from the homopolymer, the emission peak of copolymer PMAPO–VCZ in dilute solution is at about 385 nm, with a shoulder at about 431 nm (Fig. 4). When the concentration is increased, the peak at longer wavelength (431 nm) gradually improves and red shifts
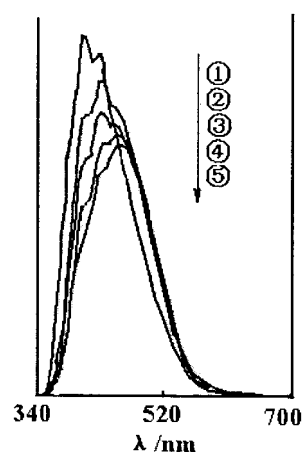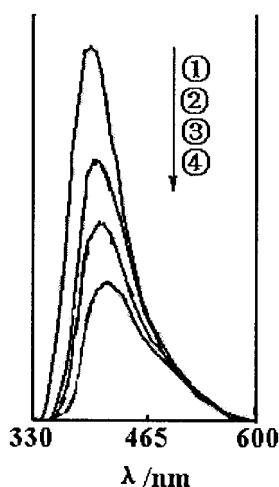

Figure 4 Fluorescence spectra of PMAPO–VCZ in THF with different concentrations (g/mL): ① 0.01, ② 0.022, ③ 0.025, ④ 0.031, ⑤ 0.036.
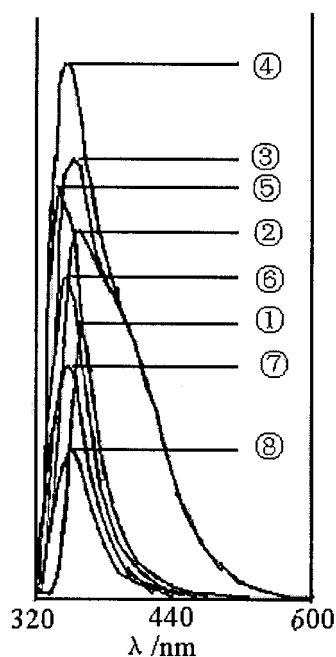
with time. These experimental facts demonstrate the presence of additional emission centers in concentrated solution of PMAPO–VCZ.[14] The emission at 385 nm originates from an excitonic state, whereas the emission of long wavelength at 431 nm can be attributed to other emission centers, which could be fluorescent dimers or other aggregate state with different degree of overlap between the different polymer chains or the separated segments on the same chains.

Interaction of copolymer PMAPO–VCZ with *N,N*-dimethylaniline (DMA)

To study the interaction between the copolymer PMA-PO–VCZ and DMA is helpful for understanding the photoelectronic properties of copolymeric materials. Figure 6 gives the fluorescence spectra of a solution of the copolymer PMAPO–VCZ in the presence of DMA. It can be seen that the emission intensity of fluorescence initially increases and then decreases with a gradual increase in the concentration of DMA. Meanwhile, the emission peaks show a blue shift and the peak breadths are narrowed. Based on the experimental facts and references, the following explanations can be given: the 1,3,4-oxadiazole unit (OXD) is an electron-deficient group and has substantial electron affinity, whereas DMA is a good electron donor, so the strong interaction between OXD and DMA occurs when DMA is gradually added to the solution of copolymers. The DMA molecule is associated with the OXD unit and the charge of DMA may then be transferred to OXD, which would lead to an increase of fluorescence intensity of the carbazole (CZ) units that are released from the actions of intramolecular or intermolecular OXD units. When the concentration of DMA increases beyond a certain limit, the excess

Figure 6 Fluorescence spectra of copolymer (PMAPO–VCZ) in THF solution with different concentrations of DMA. Concentration of copolymer (PMAPO–VCZ): 0.014 g/mL. Concentrations of DMA (mol/L): ① 0.00, ② 1.72×10^{-5}, ③ 3.44×10^{-5}, ④ 4.01×10^{-5}, ⑤ 1.55×10^{-5}, ⑥ 1.74×10^{-5}, ⑦ 2.37×10^{-5}, ⑧ 2.56×10^{-5}.

DMA units would act as a quencher to quench gradually the polymer's fluorescence.

CONCLUSIONS

The 1,3,4-oxadiazole–containing monomer PMAPO was prepared. The copolymer PMAPO–VCZ, with 1,3,4-oxadiazole ring and carbazole ring as side groups, was synthesized by radical polymerization of 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole with vinylcarbazole. In comparison with copolymer, the homopolymer of PMAPO was also synthesized.

The copolymer was stable beyond 360°C and was soluble in common organic solvents. In the solution, the photoluminescence and absorption maxima of the copolymer were at 385 and 295 nm, respectively. The emission spectra of the copolymer distinctly changed with the increase of polarity of solvents. The red shift of emission peaks was observed with the increase of solvent polarity. The copolymer emitted blue to blue-violet light and was expected to have both hole- and electron-transporting abilities because of its molecular structure containing hole- and electron-facilitating side groups.

It is a potential candidate for construction of photoluminescent devices.

Figure 5 Fluorescence spectra of P-PMAPO in THF with different concentrations (g/mL): ① 0.02, ② 0.039, ③ 0.046, ④ 0.07.

References

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackey, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. Nature 1990, 347, 539.
2. Segura, J. L. Acta Polym 1998, 49, 319.
3. Ahn, T.; Shim, H. K. Macromol Chem Phys 2001, 202, 3180.
4. Zheng, M.; Ding, L.; Gürel, E. E.; Karasz, F. E. J Polym Sci Part A: Polym Chem 2002, 40, 235.
5. Song, S. Y.; Jang, M. S.; Shim, H. K. Macromolecules 1999, 32, 1482.
6. Kim, J. J.; Kim, K. S.; Baek, S.; Kim, H. C.; Ree, M. J Polym Sci Part A: Polym Chem 2002, 40, 1173.
7. Chen, Z.; Liu, Y. Huaxue Tongbao (Chemistry) 2001, 64, 345 (in Chinese).
8. Yuan, X.; Chen, Z.; Qiao, J.; Chai, J. Spectrochim Acta Part A 2000, 56, 1869.
9. Hosangadi, B. D.; Rajesh, H. D. Tetrahedron Lett 1996, 37, 6375.
10. Pan, J.; Liu, Y.; Gao, Z. Chem J Chin Univ 1985, 6, 54.
11. Xu, D.; Yang, J.; Zhou, J.; Zhang, Y.; Hua, W. Huaxue Tongbao 1996, 10, 61 (in Chinese).
12. Hoegl, H.; Sus, O.; Neugebauer, W. Ger. Pat. 1,151,068, 1959.
13. Chen, Z.; Zhang, Z.; Zhao, T.; Bai, F.; Zhang, Y.; Wang, Z. Spectrochim Acta Part A 2001, 57, 419.
14. Zheng, M.; Bai, F.; Zhu, D. J Photochem Photobiol A: Chem 1998, 116, 143.