

New Light Emitting Materials: Alternating Copolymers with Hole Transport and Emitting Chromophores

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ABSTRACT: A new type of novel high-efficiency light-emitting nitrogen-containing poly-(phenylene vinylene) (PPV)-related copolymers, which have hole-transfer moieties such as triphenylamine (TPA) and conjugated aromatic units such as 4,4'-biphenylene, 1,4-phenylene, 2,5-dimethyl-1,4-phenylene, 1,4- or 1,5-naphthylene, and 9,10-anthrylene, was designed and synthesized by the well-known Wittig–Hornor reaction. The resulting alternating copolymers were highly soluble in common organic solvents. They can spin-cast onto various substrates to give highly transparent homogeneous thin films without heat treatment. The introduction of TPA units in the PPV backbone improved processibility and limited the π -conjugation length. Furthermore, the additional π -electron delocalization between the lone-paired electron in the nitrogen atom and π -electrons in the conjugated units contributed to the improvement of the fluorescence quantum yields of these copolymers. All these alternating copolymers except TPA–PAV have high-efficiency photoluminescence and they are very promising for light-emitting diodes (LEDs). It is very promising that TPA–PAV will emit white light when used in LED device due to the broad emission spectra. The origin of the broad spectrum is contributed by the charge-transfer complex formation, which can be proved by the absorption and emission spectra of TPA–PAV solutions. When the aromatic units were 1,4-phenylene, 1,4- or 1,5-naphthylene, 4,4'-biphenylene, and 9,10-anthrylene, respectively, with increase of the capability to accept electrons in aromatic units, the charge transfer from TPA to aromatic units occurred; consequently, the fluorescence quantum yield decreased. The introduction of the alkoxy-substitute group on the aromatic units in the polymer backbone caused the red shift of the absorption and emission spectra of the copolymers due to the stronger delocalization of the π -conjugated system. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3351–3358, 1999

Key words: triphenylamine; PPV; charge-transfer complex

INTRODUCTION

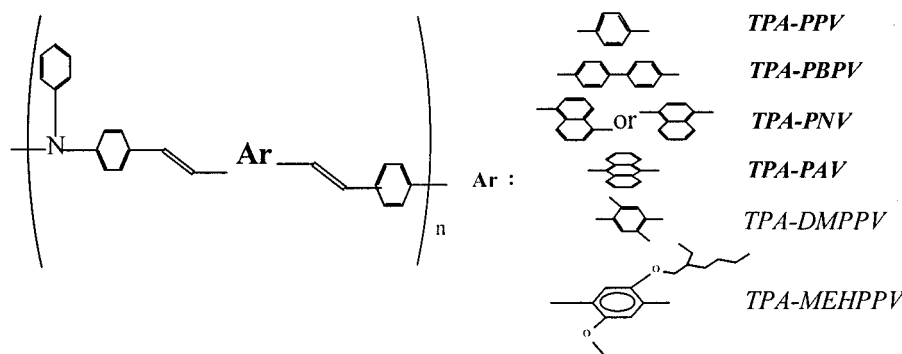
The high photoluminescence observed in many organic semiconductors raised the possibility of

solid-state light emission under an applied electric field. Light-emitting diodes (LEDs) were first fabricated from small organic molecules.^{1,2} These systems present the main disadvantage that active molecules can recrystallize during device operation, leading to poor device stability. The use of conjugated polymers in LEDs based on poly-(phenylene vinylene) (PPV) was first realized by the Cambridge group in the early 1990s.³ Since then, a great number of different polymer materials suitable for LEDs have been synthesized and

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Scheme 1 The chemical structures of the alternating copolymers.

developed.^{4–7} However, many of these polymers contained saturated and nonconjugated spacer groups between the chromophores which act as a barrier to the injection and mobility of the charge carriers, leading to the requirement of materials with high threshold voltages that generally damage the polymeric materials. Therefore, it seemed desirable to develop new series of polymers requiring low-drive voltages with predictable emission wavelengths.

On the other hand, although the solubility of PPV can be achieved by introducing solubility-enhancing side chains on the phenylene ring⁸ or by inserting solubility-enhancing groups in the backbone.⁹ Many single-layer LEDs based on these polymers often show higher driving voltage and lower efficiency because of unbalanced charge injection. So, an additional hole-transporting layer, mostly triarylamine derivatives, is used to fabricate multilayer LEDs^{10,11} due to their high carrier mobility. A drawback of this method is that both layers are soluble in common organic solvents like benzene or chloroform, which generally leads to rough interfaces between the two layers upon spin coating. Additionally, triarylamine derivatives have low glass transition temperatures and are easy crystallized from an organic layer under continuous operation or storage. Thus, our purpose was to incorporate these hole-transporting compounds into the PPV backbone. In this article, we deal with the synthesis, characterization, and optical properties of the nitrogen-containing PPV-related copolymers in the main chain, which have hole-transfer moieties and conjugated aromatic units such as 4,4'-biphenylene, 1,4-phenylene, 2,5-dimethyl-1,4-phenylene, 1,4- or 1,5-naphthylene, and 9,10-anthrylene. The chemical structures of these six copolymers are shown in Scheme 1.

EXPERIMENTAL

Measurements

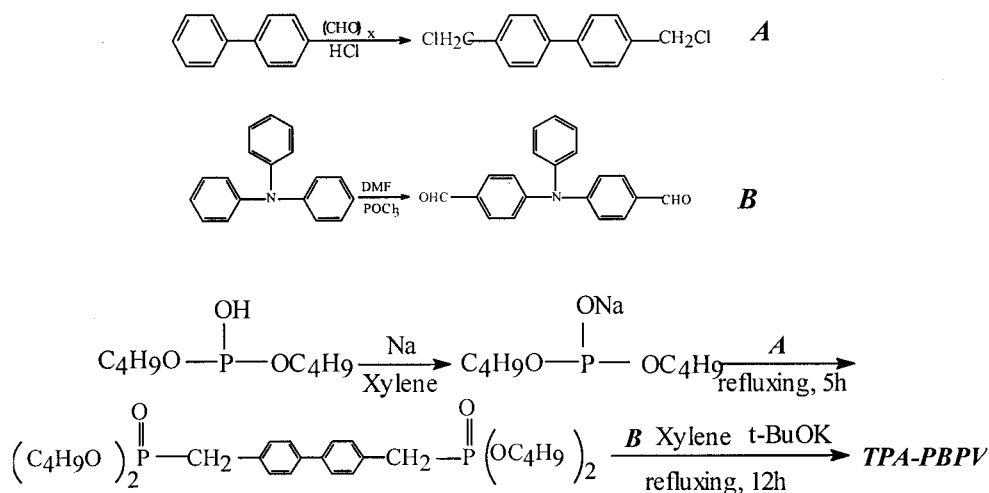
IR spectra were recorded as KBr pellets on a 1700 FTIR spectrometer. ¹H-NMR spectra were collected on a Varian XL-200 spectrometer with *d*-chloroform as a solvent and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. UV spectra were taken on a Hitachi 340 UV-vis spectrometer. The fluorescence spectra were measured on a Hitachi MPF-4 fluorescence spectrophotometer. All processing steps and measurements mentioned above were carried out in an air atmosphere at room temperature.

Thermogravimetric analysis was performed on a Perkin–Elmer Thermal Analysis System 7. The sample was recorded in a nitrogen atmosphere at a heating rate of 10°C/min. The fluorescence quantum yield in solution was determined from corrected spectra against Perylene¹² as a standard ($\phi_{\text{FL}} = 94\%$) excited at 405 nm.

Materials

Cyclohexane, benzene, tetrahydrofuran, chloroform, and acetonitrile were purchased from the Beijing Chemical Plant (Beijing, China) without further purification prior to use. Interference fluorescence was not observed under the experimental conditions for all the reagents used.

Dibutylphosphite and *p*-xylylene dichloride were purchased from Acros Organics N. V. (Gul, Belgium) and Tokyo Kasei Kogyo Co., (Japan) respectively. Triphenylamine, phosphoryl chloride, biphenyl, naphthalene, anthracene, *p*-xylene, paraformaldehyde, concentrated hydrochloric acid, and glacial acetic acid were purchased from the Beijing



Scheme 2 The synthesis route of the TPA-PBPV.

Chemical Plant. The required solvents were purified according to conventional methods before use.

Monomer Synthesis

The synthesis of monomers was carried out as shown in Scheme 2 including the bischloromethylation of aromatic compounds (A), the dialdehydation of triphenylamine (B), and the preparation of the bisdibutylphosphate. One example of the synthesis of the TPA-PBPV is described as follows:

4,4'-Bis(chloromethyl)biphenyl

A mixture of biphenyl (15.4 g, 0.1 mol), paraformaldehyde (12 g, 0.4 mol), 98% ZnCl_2 (24 g, 0.16 mol), and 11 mL CCl_4 was saturated with dry HCl gas for 0.5 h under stirring at room temperature followed by addition of 24 mL glacial acetic acid and 11 mL concentrated hydrochloric acid. The mixture was heated to 50–60°C and kept saturated with dry HCl for 3 h. After standing for 24 h at room temperature, the solution was poured into 400 mL cold water, washed with CCl_4 , NaHCO_3 , distilled water, and brine for three times, respectively, and purified by repeated crystallization from alcohol to give 9 g ($p\text{-ClCH}_2\text{C}_6\text{H}_4$)₂; mp: 136°C.

Triphenylamine Dialdehyde

To 12.3 mL of *N,N*-dimethylformamide and 5 g triphenylamine cooled to 0°C, 14.7 mL of phosphoryl chloride was added dropwise under stirring followed by refluxing for 3 h. After standing

for 10 h at room temperature, the mixture was poured into 300 mL cold water and neutralized by a 20% NaOH solution and then filtered. The crude product was purified by silica gel column chromatography (elute: ethyl acetate/petroleum ether = 1/2). Yield: 75%. Mp: 140°C. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.1–7.2 (m, 4H); 7.3–7.5 (m, 5H); 7.7–7.8 (m, 4H); 9.8–10.0 (s, 2H).

Polymer Synthesis

The polymer was synthesized by the modified procedures described in the literature.^{13,14} Metallic sodium (0.23 g, 0.01 mol) was placed into a three-necked round-bottom flask, provided with a dropping funnel, a sealed stirrer, and a reflux condenser closed with a calcium chloride tube; 100 mL dry toluene was placed into the flask, and while the liquid was being gently refluxed with agitation, dibutylphosphite (2 g, 0.01 mol) was added dropwise over 20–30 min, after which the refluxing and stirring were continued until the sodium was completely dissolved. This reaction generally required 2–3 h. After the solution was cooled to room temperature, 4,4'-bis(chloromethyl)biphenyl was added and refluxed for 5 h. Triphenylamine dialdehyde (1.5 g, 0.005 mol) was added at room temperature. Then, the mixture was stirred at 110°C under Ar until dissolution was complete. The solid *t*-BuOK (1.68 g, 0.015 mol) was added in one portion. After 12 h at reflux, the solution was removed by rotary evaporation. The residue was dissolved in chloroform, filtered, and precipitated into methanol to give a yellow product.

Table I Thermal and Optical Properties of the Alternating Copolymers' Examination

	T_g (°C)	T_{ID}^a (°C)	UV λ_{max} (nm) In Benzene	PL λ_{max} (nm)		Q_{eff}^b
				In Benzene	Film	
TPA-PBPV	91	258	335, 375	455, 487 (sh)	490, 510 (sh)	0.7
TPA-PPV	146	300	420	470, 500 (sh)	510, 560 (sh)	1.0
TPA-PNV	116	254	414	507, 545 (sh)	530, 570 (sh)	0.9
TPA-PAV	135	262	320–420	430–600	570	0.07
TPA-DMPPV	125	271	411	480, 507 (sh)	500, 530 (sh)	0.9
TPA-MEHPPV	61	270	437	496, 525 (sh)	565, 600 (sh)	0.8

^a Temperature at which initial loss of mass was observed.

^b The fluorescence quantum yield in benzene relative to perylene excited at 405 nm.

RESULTS AND DISCUSSION

Synthesis and Thermal Properties

The synthetic strategy is based on step-growth polymerization through PO-activated olefination of dialdehydes with primary or secondary bisphosphonates (Horner reaction). The monomers, namely, the bisphosphonates and the dialdehydes of triphenylamine, can easily be prepared by conventional organic reactions. The synthetic approach to TPA-PBPV is sketched in Scheme 2. Thus, as shown in Scheme 2, 4,4-biphenyl bis-dibutylphosphate was synthesized by chloromethylation of biphenyl followed by the Arbuzov reaction. Triphenylamine can be directly functionalized into the triphenylamine dialdehyde by the Vilsmeier reaction. The polymerization was carried out in a concentrated toluene solution using potassium *tert*-butylate as the condensing agent to give yellow products.

The chemical structures of the resulting copolymers were identified by FTIR and ¹H-NMR. Comparison of the FTIR spectra of TPA-PBPV and the triphenylamine dialdehyde monomer showed the formation of the designed polymer. The peaks at 1690 cm⁻¹, which are expected for the aldehyde carbonyl-stretching band of the dialdehyde monomer, drastically decreased. Additionally, the FTIR spectra of the copolymer show a peak at 965 cm⁻¹ that corresponds to the stretching of *trans*-vinylene C—H bonds, whereas no peak corresponding to the stretching of *cis*-vinylene bonds can be seen in the 890–900 cm⁻¹ region. This clearly indicates that the vinylenes newly formed are mainly of *trans*-configuration. The molecular structure of the copolymers can also be confirmed from ¹H-NMR spectra. In the ¹H-NMR spectrum of TPA-PBPV,

the absence of peaks at about 6.5 ppm also indicates that no *cis*-vinylene bonds are present.

All these synthesized copolymers were highly soluble in common organic solvents such as tetrahydrofuran and chloroform. This implies that the introduction of TPA units in the rigid polymer backbone can reduce the chain stiffness and increase the polarity of the polymer, thus enhancing the solubility of PPVs. They can spin-cast onto various substrates to give highly transparent homogeneous thin films without heat treatment.

The thermal properties of the designed copolymers were evaluated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The results are presented in Table I. All the polymers showed good thermal stability up to 250°C. They have T_g values in the range of 60–150°C. An increase in the T_g can be achieved by decreasing the length of the side chains. TPA-MEHPPV has the lowest T_g value because of its long side chains on the phenylene ring. From TPA-MEHPPV to TPA-DMPPV and to TPA-PPV, with decrease of the length of the side chains, the T_g values increased from 61 to 125°C and to 146°C. The T_g value of TPA-PAV was higher than that of TPA-PBPV, indicating more rigidity of TPA-PAV.

Optical and Photoluminescence Properties

It is known that the fluorescence quantum yield of light-emitting materials strongly affects electroluminescence efficiencies. Thus, we first examined the relative fluorescence quantum efficiencies of these copolymers in benzene solutions. The results are listed in Table I. The novel copolymers show high values of a photoluminescence quantum yield except for TPA-PAV. This is directly related to the chemical structures of these nitro-

gen-containing PPV-related copolymers. The introduction of the TPA unit into the polymer rigid backbone interrupts the regular π - π conjugation system of the PPV backbone, which prevents the excitons from migrating to traps and, therefore, the ratio of the nonradiative process is reduced. On the other hand, the additional π -electron delocalization between the lone-paired electron in the nitrogen atom of TPA and the π -electrons in the conjugated units changed the conjugation system of the copolymer backbone and, therefore, contributed to the improvement of the fluorescence quantum yields of these copolymers. So, they are unlike the reported copolymers⁹ that contained saturated and nonconjugated spacer groups between the chromophores which act as a barrier to the injection and mobility of the charge carriers, leading to the requirement of materials with high threshold voltages that generally damage the polymeric materials. Their high photoluminescence quantum yields indicate their promising application in light-emitting devices. As to the TPA-PAV, its fluorescence quantum yield in benzene decreased sharply. This is due to the formation of a charge-transfer complex, which will be discussed in the following. To reach the unity of the measurement among the six copolymers, the same standard and excited wavelength were used. In fact, there was only the charge-transfer complex emission for TPA-PAV to be excited at this excitation wavelength. Consequently, the measured value of the fluorescence quantum yield was lower than was the actual one.

The UV-vis absorption and fluorescence emission of TPA-PPV, TPA-DMPPV, and TPA-MEHPPV are shown in Figure 1 and the results are listed in Table I. Both the maximum of absorption and emission wavelengths of TPA-MEHPPV appear at the longest wavelength among the three copolymers. The alkoxy-substituted side chains on the phenylene ring have two opposite effects to the conjugation system of the polymer backbone. On the one hand, the introduction of the side chains twisted the polymer backbone and, consequently, decreased the effective conjugation length, which caused the blue shift of absorption and emission spectra. On the other hand, the introduction of the donating-electron alkoxy-substituted units can make the delocalization of the π -conjugation system stronger, which caused the red shift of absorption and emission spectra. Obviously, for the TPA-PPV-related copolymers, the latter effect surpassed the former. Compared with MEH-PPV ($\varphi_{\text{eff}} = 0.35$ in chloroform, $\lambda_{\text{max}}^{\text{em}} = 570$ nm in

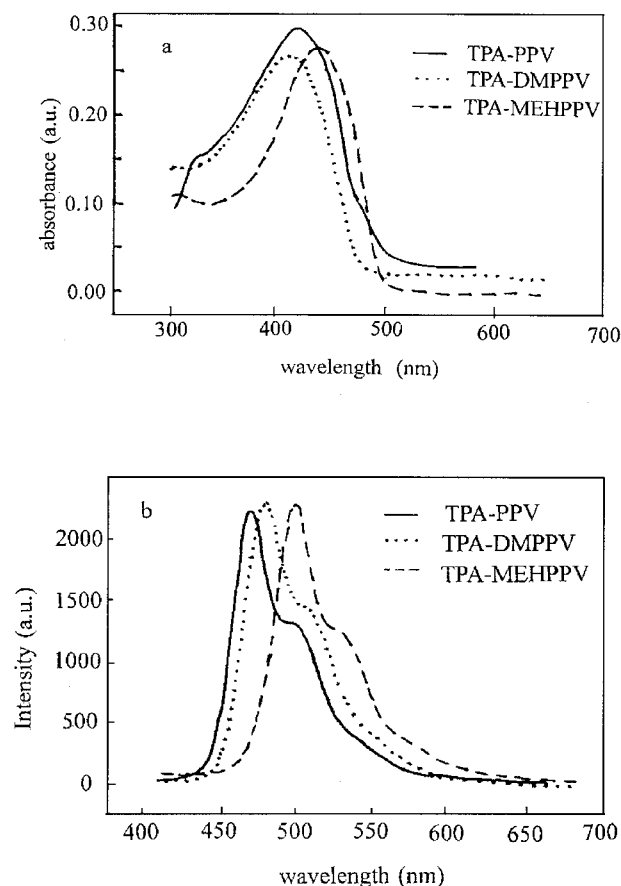


Figure 1 (a) Absorption and (b) emission spectra of TPA-PPV, TPA-DMPPV, and TPA-MEHPPV solutions (normalized). Exciting wavelength: 405 nm; concentration: $2 \times 10^{-5}M$.

chloroform), which recently, is mostly used as the active layer in LEDs and has been proven to be a very interesting material because of its high PL efficiency and its good solubility in the conjugated form; TPA-MEHPPV has higher fluorescence efficiency and more blue-shifted emission. The emissions of the three copolymer solid films were also examined. The results (Table I) showed about a 30-nm red shift compared with that in diluted solution due to the aggregate or the interaction of interchains.

Figure 2 shows the UV-vis absorption and emission spectra of the four copolymers TPA-PBPV, TPA-PPV, TPA-PNV, and TPA-PAV. As shown in the absorption spectra, two maximum absorption wavelengths of the TPA-PBPV are located at 335 and 375 nm, which are attributed to the π - π^* transition of the π -conjugated segment, while the maximum absorption wavelength of TPA-PPV and TPA-PNV were at 420 and 414

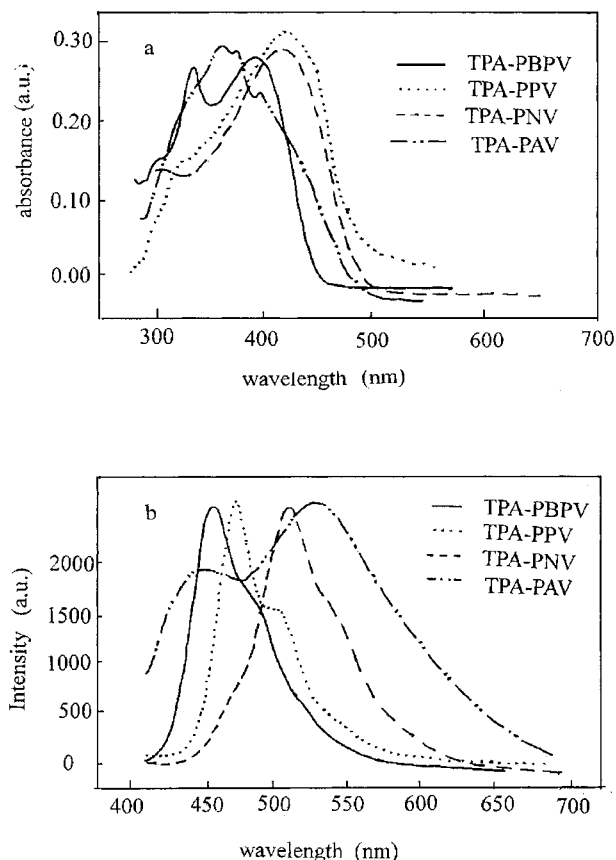


Figure 2 (a) Absorption and (b) emission spectra of TPA-PPV, TPA-PBPV, TPA-PNV, and TPA-PAV (normalized). Exciting wavelength: 405 nm; concentration: $2 \times 10^{-5}M$.

nm, respectively. The fluorescence emission spectra show shifts similar to those observed in the absorption spectra. The solution of TPA-PPV and TPA-PNV show a very intense green light that peaked at 470 and 507 nm. The emissions are about 30 nm red-shifted in solid films (Table I). In contrast, the maximum emission wavelength of TPA-PBPV in a diluted solution and in solid films appear peaked at 455 and 490 nm, resulting in a blue shift of about 20 nm compared with that of TPA-PPV and TPA-PNV. The maximum emission wavelength of the π -conjugated polymers depends on both the degree of conjugation and the effective conjugation length. As for TPA-PBPV, the 4,4'-biphenylene on the polymer backbone disturbs the coplanarity of the π -conjugated segment and, consequently, reduces the effective conjugation length, which results in a blue shift. The electroluminescent properties of these copolymers were also characterized and the results are listed in our other articles.^{15,16}

In the case of TPA-PAV, the absorption spectrum is broad and has a long tail, which may indicate the formation of a charge-transfer complex. The emission spectrum is also broad and flat in the region from 430 to 600 nm, which is an advantage in emitting white light (close to sunlight). The formation of the charge-transfer complex can be confirmed from the absorption and emission spectra of TPA-PAV in different solvents (Fig. 3). TPA-PAV has almost the same vibronic structure absorption spectra in different solvents, with very long tailed peaks beginning at 550 nm and peaking at 360 nm.

The shoulder at 450 nm of the charge-transfer complex is obvious in all the different solvents. The emission spectra changed much with the polarity of the solvents. From benzene to acetonitrile, the peak at the long wavelength, which was attributed to the charge-transfer complex, red-shifted gradually and became stronger due to more stability of the charge-transfer complex in polar solvents. The emission spectra in benzene

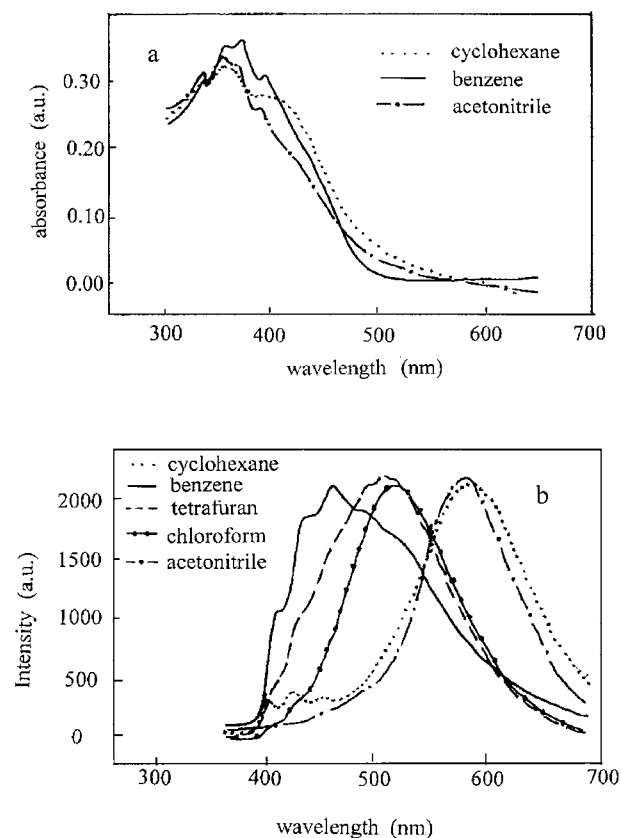


Figure 3 (a) Absorption and (b) emission spectra of TPA-PAV in different solvents (normalized). Exciting wavelength: 350 nm; concentration: $2 \times 10^{-5}M$.

has a long-tailed peak at 506 nm of the charge-transfer complex and three obvious well-defined peaks at 405, 428, and 453 nm, which were ascribed to the normal emission of TPA-PAV. With increase of the solvent's polarity, the three peaks at the short wavelength decreased gradually and almost disappeared in acetonitrile. For emission in the cyclohexane, which is a nonpolar solvent, the intensity of the emission of the charge-transfer complex at 586 nm is much stronger than that of the three peaks at the short wavelength, although they also can be seen. Unlike the benzene, cyclohexane is not a good solvent for TPA-PAV. The polymer chain is more kinked in cyclohexane than in benzene, which caused the stronger interaction between TPA and 9,10-anthrylene, with the subsequent easy formation of the charge-transfer complex.

The formation of the charge-transfer complex can be further confirmed by the emission of TPA-PAV in benzene when excited at different wavelengths. Figure 4 demonstrates the emission of TPA-PAV (a) in concentrated and (b) in diluted solutions excited at 350 and 405 nm, respectively. In the diluted solution, both the three well-defined peaks at the short wavelength ascribed to the normal emission and the peak of the charge-transfer complex located at a longer wavelength can be seen and both of them are main parts when excited at 350 nm, while the emission of the charge-transfer complex becomes the main part and the peaks at the short wavelength become structureless when excited at 405 nm. However, in the concentrated solution excited at 350 nm, the normal emission at the short wavelength can be seen faintly, while when the concentrated solution is excited at 405 nm, the emission of the charge-transfer complex can only be observed and the normal emission completely disappeared. These phenomena are due to the easier formation of the charge-transfer complex and energy transfer to the lower level of the charge-transfer band in the concentrated solution. In the diluted solution, charge transfer occurred in the intrachains, but in the concentrated solution, both the intrachain and interchain charge-transfer complexes exist.

Compared with the 1,4-phenylene, 1,4- or 1,5-naphthylene, and 4,4'-biphenylene, 9,10-anthrylene has a stronger ability to accept electrons. So, from TPA-PPV, TPA-PNV, TPA-PBPV to TPA-PAV, with increase of the capability of the aromatic units to accept electrons, the charge transfer from TPA to aromatic units more easily

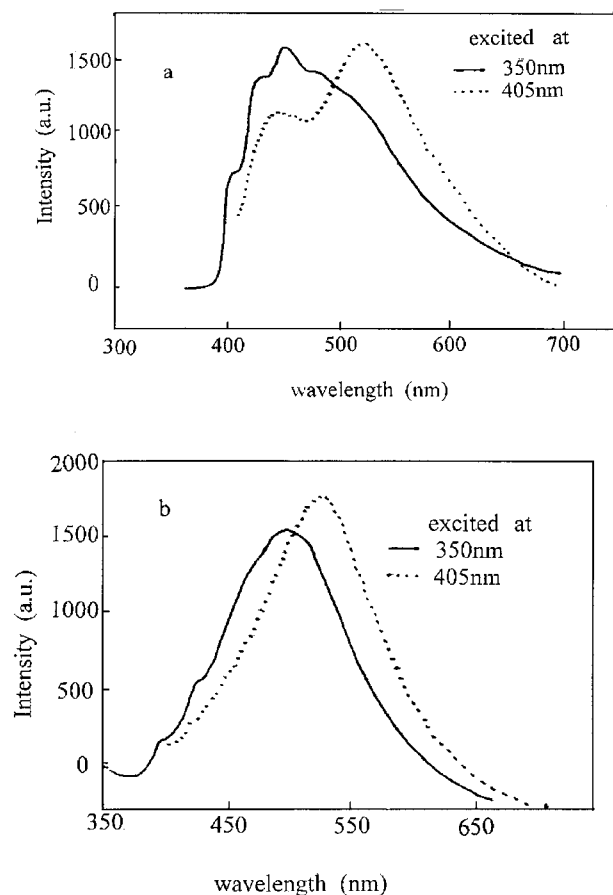


Figure 4 Emission of TPA-PAV in (a) diluted (concentration: $2 \times 10^{-5} M$) and (b) concentrated solution (concentration: $2 \times 10^{-3} M$) excited at different wavelengths (normalized).

occurred, which, consequently, caused decrease of the fluorescence quantum yield. From the above, we can conclude that when we design a new copolymer the interaction between the chromophore's functional group should be considered. The balance between the donating and accepting electron capability of each functional group should be kept.

CONCLUSIONS

In summary, a new class of nitrogen-containing PPV-related copolymers with a uniform π -conjugated segment regulated by TPA units was synthesized by the well-known Wittig-Horner reaction. These new copolymers have hole-transfer moieties and conjugated aromatic units. The resulting alternating copolymers have excellent sol-

ubility in common organic solvents. They can spin-cast onto various substrates to give highly transparent homogeneous thin films. The introduction of TPA units in the PPV backbone improved the solubility and processibility and limited the π -conjugation length. Furthermore, the additional π -electron delocalization between lone-paired electrons in the nitrogen atom and π -electrons in the conjugated units contributed to the improvement of the fluorescence quantum yields of these copolymers. All these alternating copolymers except TPA-PAV have high-efficiency photoluminescence and they are very promising for LEDs.

TPA-PAV is a very promising polymer to emit white light when used in an LED device due to the broad emission. The origin of the broad spectrum is contributed by the formation of the charge-transfer complex, which can be proved by the absorption and emission spectra of the TPA-PAV solutions. When the aromatic units were 1,4-phenylene, 1,4- or 1,5-naphthylene, 4,4'-biphenylene, and 9,10-anthrylene, respectively, with increase of the capability of aromatic units to accept electrons, the charge-transfer more easily occurred, which, consequently, caused decrease of the fluorescence quantum yield. The introduction of the alkoxy-substitute group on the aromatic units in the polymer backbone caused the red shift of the absorption and emission spectra of the copolymers due to the stronger delocalization of the π -conjugated system.

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