

Synthesis and Fluorescence of Polymeric Triphenylamine Obtained by Oxidative-Coupling Polymerization

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ABSTRACT: We prepared triphenylamine (TPA)-containing polymers by a direct oxidative-coupling method, which showed high thermostability, good solubility, high quantum efficiency, and blue light emission. The polymers are characterized by Fourier transform infrared spectroscopy, $^1\text{H-NMR}$, ultraviolet-visible spectroscopy, thermogravimetric analysis, elemental analysis, and fluorescence spectra. The homopolymeric TPA (PTPA) was fairly soluble in CCl_4 and toluene, with a quantum yield of 0.38 relative to Rhodamine B in toluene solution, and showed blue light emission in solid-state film. The TPA-stilbene copolymers were more soluble than the PTPA and showed violet to green light emission in solid-state film, depending on the TPA moiety contents, from which a pure blue light emission could be obtained. The emitting quantum efficiency of the copolymers measured in toluene solution was from 0.57 to 0.78 relative to Rhodamine B. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2718–2724, 2002

Key words: hyperbranched; conjugated polymers; copolymerization; fluorescence

INTRODUCTION

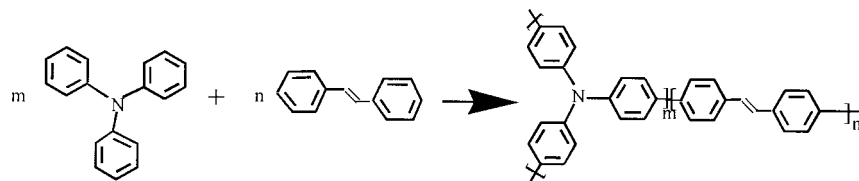
Organic electroluminescent (EL) devices have attracted wide attention because of their potential application as large-area light-emitting displays with low driving voltage, high efficiency, and high brightness. In organic EL devices, triphenylamine (TPA) and its derivatives have been extensively made as hole-transporting layers (HTLs) due to their high carrier mobility and amorphous film-forming ability. However, the process of crystal growth of the vapor-deposited flat and amorphous film of diphenylamine (DPA), a TPA dimer, was observed even at ambient temperature.¹ It means that the morphological change of deposited TPA and its derivatives result from operation heat and molecular migration promoted by the molecular motion near glass-transition tempera-

ture (T_g) would degrade the EL devices then shorten their lifetime. Therefore, the high T_g and high molecular weight of HTL materials are required for the long-term stability of the EL devices. Polymeric materials have another advantage of processibility, which is fabricated just by spin-coating from solution. So far, oligomers, homopolymers, and copolymers based on TPA have been prepared by different methods to improve EL devices. A new branched polytriphenylamine (PTPA) was prepared by the Grignard reaction.² Oligomeric TPAs were prepared through an Ullmann coupling reaction between arylamine and aryl iodide, which had higher T_g and offered EL devices excellent stability at high temperatures.³ A TPA homopolymer was prepared by nickel-catalyzed polycondensation of Grignard reagents.⁴ Silicone cross-linked TPA was used as a HTL in light emitting devices (LEDs), and a high forward-light output was obtained.⁵

TPA copolymers can be used as both hole-transporting and emitting materials in LED.^{6–8}

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PTPA: $n = 0$; copolymer: $m, n \neq 0$

Scheme 1 PTPA $n = 0$; copolymer $m, n \neq 0$.

The copolymer of TPA and bisquinoline obtained from Buchward coupling possesses excellent thermal stability and good electron injecting and transporting ability.⁶ The copolymers with TPA in a poly(phenylenevinylene) (PVA) backbone prepared by the Wittig-Hornor reaction have excellent solubility and a high EL efficiency as an emitting layer in LED.⁷

In contrast to the complicated synthetic procedure of polymeric TPA, facile and economic preparation is necessary for the practical application of LED. The Scholl reaction, or oxidative-coupling reaction, is a facile method used to prepare aromatic conjugated polymers and which directly uses TPA and stilbene as monomers without introducing bifunctional groups for polymerization as the synthetic procedure of polymeric TPA does.⁹ The electron-rich TPA molecule can afford the reaction to form a thermally and electrochemically stable polymer. In this article, we report on the facile synthetic method of the TPA-containing polymer as shown in Scheme 1. The synthesis, characterization, solubility, stability, absorption, and fluorescence spectra are described.

EXPERIMENTAL

Materials and Preparation of the Copolymers

All chemicals and solvents were commercial agents; TPA–stilbene copolymers were prepared as reported previously.¹⁰

Preparation of PTPA

FeCl_3 (1.3 g, 8 mmol) TPA (0.5 g, 2 mmol) in 15 mL chloroform were stirred in a three-necked flask equipped with condenser, gas inlet, and electrical magnetic stirrer under an argon atmosphere. The reaction was continued overnight at room temperature. Then, FeCl_3 was filtered off, and the filtrate was poured into 75 mL of methanol. The precipitated product was collected by filtration, washed with methanol several times to remove the monomers and low-molecular-weight molecules, and dried in an oven below 60°C. The weight of the recovered homopolymeric TPA was 0.22 g, (yield-44%). Its inherent viscosity in toluene at 30°C was 0.33 dL/g.

ELEM. ANAL. Calcd: N, 5.76%; C, 88.9%; H, 5.35. Found: N, 5.7%; C, 88.8%; H, 5.5%.

Table I Synthesis of TPA-Containing Polymers

	Polymer				
	I	II	III	IV	PTPA
Feed ratio (S/T, mol) ^a	1 : 1	2 : 1	1 : 2	1 : 1	0 : 1
Reaction time (h) ^b	16	24	24	24	24
η_{inh} (dL/g)	0.36	0.48	0.49	0.52	0.33
TPA unit (mol %) ^c	43	51	74	62	100

^a Unit ratio of stilbene and triphenylamine.

^b Inherent viscosity.

^c Calculated from nitrogen content.

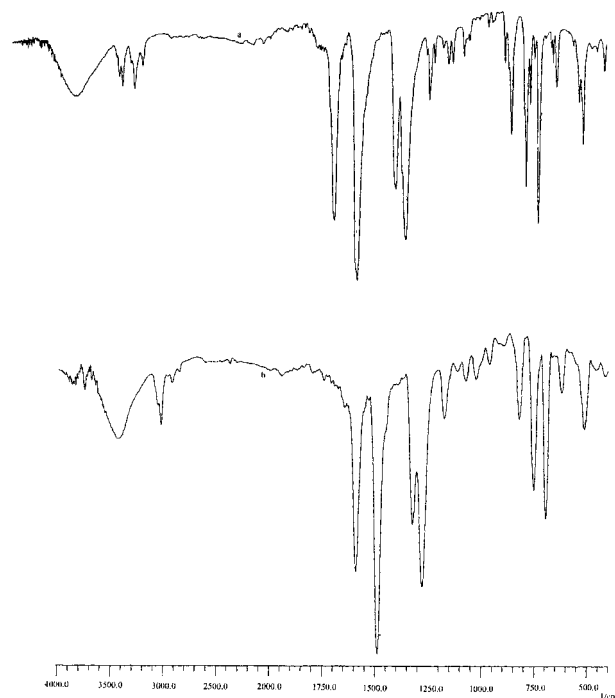


Figure 1 FTIR spectra of polymeric TPA (top) and copolymer **III** (bottom).

The number-average molecular weight (M_n) measured from gel permeation chromatography (GPC) was 2000, the weight-average molecular weight (M_w) was 2300, and the polydispersity was 1.35.

Instrumentation and Measurement

Ultraviolet-visible (UV-Vis) absorption spectra were measured on a Shimadzu UV-160A spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 170SX FTIR spectrometer. $^1\text{H-NMR}$ was performed on a Mercury VX300 spectrometer. Fluorescence spectra were measured with a fluorescence spectrophotometer (RF-5301PC). Quantum yield was measured with Rhodamine B as a standard. Thermal analyses were conducted on Shimadzu DT-40 instrument. Solubility was measured as previously reported.¹⁰

RESULTS AND DISCUSSION

Synthesis

The three benzene rings on the TPA molecule have equal reactivities and abilities to form cation radicals, which are the reactive centers of chain

propagation. Therefore, both the homopolymer and the copolymers can be highly branched molecules. However, the deep investigation of the branch structure of the polymers is still under development.

The copolymerization of TPA and stilbene incorporates TPA moieties and double carbon-carbon bonds into main chains and offers larger molecular weight than the homopolymer. The inherent viscosity measurement shown in Table I illustrates that the copolymers had higher molecular weights than the PTPA. The molecular weight of Copolymer **III** as measured by GPC was $M_n = 4200$, $M_w = 5700$, and polydispersity = 1.35 about two-fold of PTPA.

On the other hand, both TPA and stilbene could self-polymerize in this condition and had ability to join polymer chain. The results listed in Table I show that the contents of the TPA moieties calculated from nitrogen content were in the range of 43–74%, increasing with the TPA feed ratio and reaction time. The composition changed with the feed ratio and polymerization time. This means the two moieties statistically linked on the polymer chains.

Characterization

The FTIR spectrum of PTPA (Fig. 1) exhibited unsaturated $\text{C}=\text{C}$ vibration at 1500 and 1600 cm^{-1} , saturated $\text{N}-\text{C}$ stretching at 1320 cm^{-1} , and the characteristic vibration of mono- and 1,4-substitution at 700, 750, and 820 cm^{-1} .

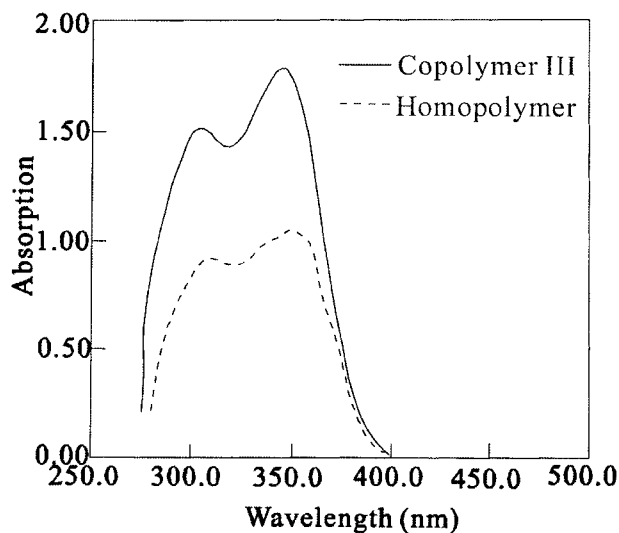


Figure 2 UV-Vis spectra of copolymer **III** and the TPA homopolymer in toluene.

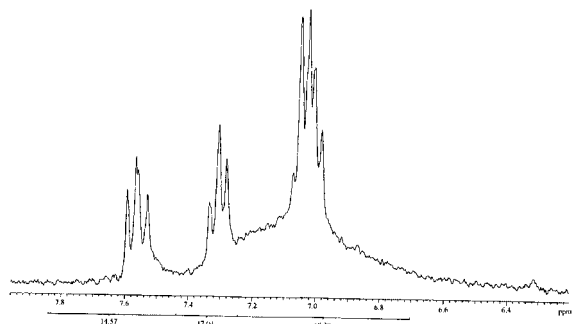


Figure 3 $^1\text{H-NMR}$ spectrum of copolymer **III**.

The FTIR spectrum of copolymer **III** (Fig. 1) showed all the vibration bands of PTPA and a sharp band at 960 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene group, indicating the structure of *trans*-stilbene.

The UV-Vis spectra of PTPA and copolymer **III** in toluene solution are shown in Figure 2. The homopolymer had two absorption bands at 310 and 353 nm, and the copolymer had absorption at 315 and 352 nm, very similar absorption in this case. In comparison to the monomer TPA and stilbene, which have maximum absorption bands at 296 and 300 nm, respectively, the absorption of the polymers had a red shift about 50 nm. This means that a larger conjugative π system formed because of the polymerization.

In the $^1\text{H-NMR}$ spectrum of copolymer **III** (Fig. 3), all the signals positioned at $\delta = 6.9$ to 7.6 ppm confirmed the aromatic structure of the copolymer. Here, the multiple signals at 6.9 – 7.05 ppm, the triplets at 7.23 – 7.33 ppm, and the quaternary signals at 7.53 – 7.59 ppm were assigned to the hydrogen of stilbene, the monosubstituted benzene of TPA, and the paralinked benzene ring of the TPA moieties, respectively.

Solubility

The solubilities of PTPA and the TPA–stilbene copolymer **III** measured at room temperature are listed in Table II. PTPA had a solubility of 0.48

Table II Solubility of Copolymer **III** and PTPA (g/100 mL)

Solvent	Toluene	CCl_4	Acetone	DMSO	Ethanol
Copolymer III	1.41	1.61	0.33	0.59	0.09
PTPA	0.48	0.41	0.14	0.19	0.02

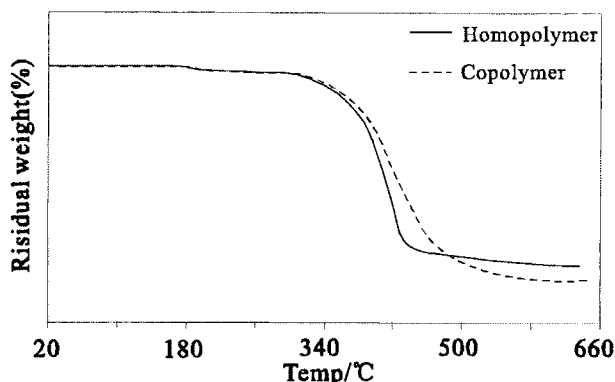


Figure 4 TGA curves of the homopolymeric TPA and copolymer **III**.

g/100 mL in toluene and 0.41 g/100 mL in carbon tetrachloride, whereas copolymer **III** had a value of 1.4 and 1.6 g/100 mL in toluene and carbon tetrachloride, respectively. The results illustrate that copolymerization improved the solubility of the TPA-containing polymer.

Because there were no alkyl or alkyloxy groups linked in the main chain or side chain, we think the solubility was good for these rigid aromatic conjugated TPA-containing polymers. These results may be attributed to its highly branched structure.

Thermoanalyses

The thermogravimetric analysis (TGA) curve (Fig. 4) revealed very low ($< 1\%$) weight loss from

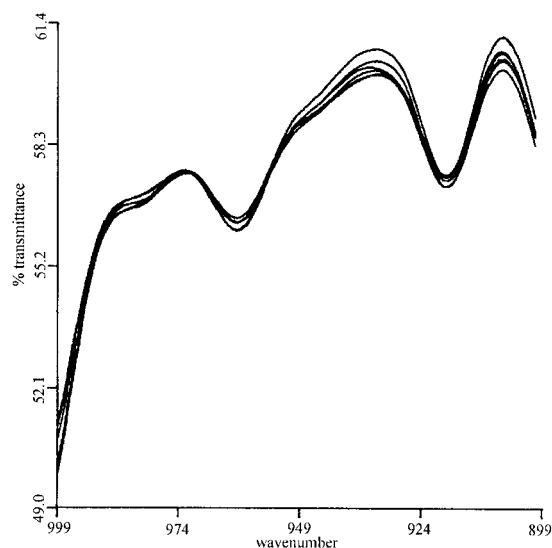


Figure 5 The band at 960 cm^{-1} of the FTIR spectra of copolymer **III** exposed under UV light. Radiation time (upward): 0 min, 1 min, 5 min, 1 h, and 10 h.

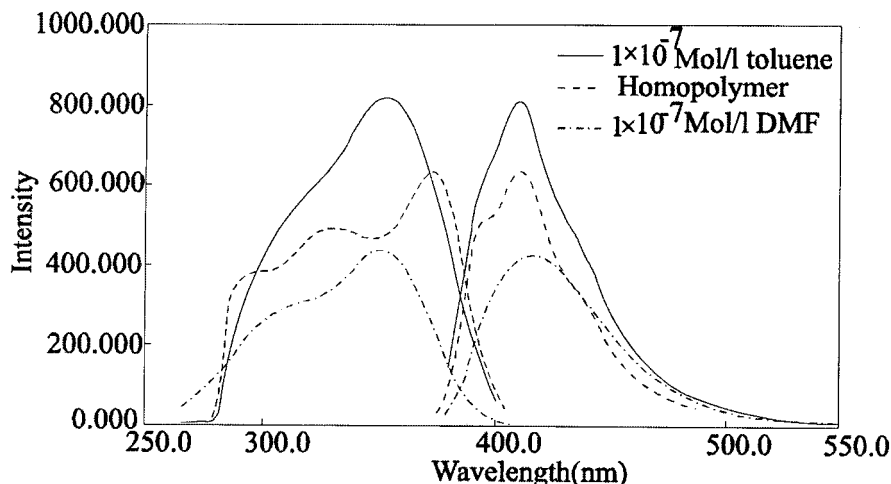


Figure 6 Fluorescence spectra of copolymer **III** and PTPA in solution (slit width = 3 nm).

173 to 293°C and a starting decomposition temperature of 300°C for PTPA. Copolymer **III** had a very similar thermostability to PTPA. Differential scanning calorimetry determination showed transition temperatures of 215 and 220°C for the homopolymer and copolymer **III**, respectively. The thermoanalysis results indicated that the TPA-containing polymers had high thermostability and could offer good performance in an EL device.

Ultraviolet (UV) Light Stability

It has been reported that *trans-cis* photoisomerization of stilbene takes place in the presence of TPA.¹¹

In the copolymers incorporated TPA and stilbene moieties on the main chain, whether the TPA moieties promote the *trans-cis* isomerization of the stilbene moieties? If the *cis-trans* transformation takes place, the quantum yield of the copolymers would decrease dramatically under radiation because the quantum yield of *cis*-stilbene is nil at room temperature. To explore whether the *trans-cis* photoisomerization took place under light, a sample of copolymer **III** was exposed under UV light of 200–400 nm for 10 h, and the characteristic vibration of the *trans*-vinylene group, the band at 960 cm^{-1} , in the FTIR spectrum was measured. The results shown in Figure 5 illustrate that the band was

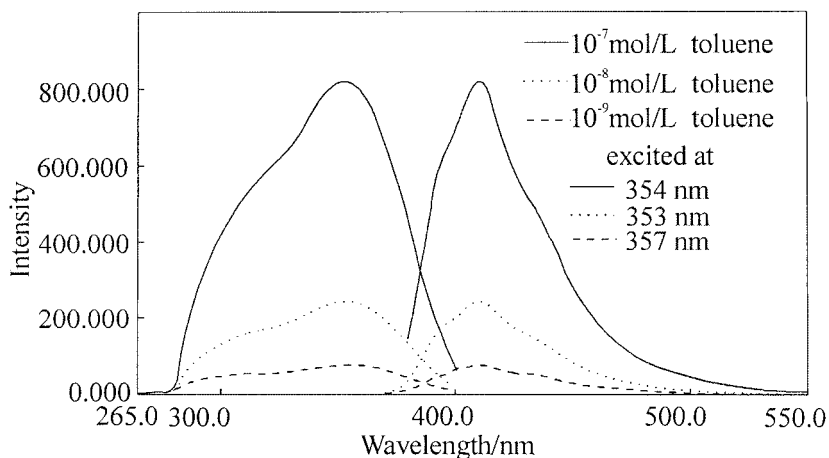


Figure 7 Fluorescence spectra of copolymer **III** in different concentrations of toluene solution (slit width = 3 nm).

Table III PL Properties of TPA-Containing Polymers

	Polymer				
	I	II	III	IV	PTPA
TPA unit (%)	43	51	74	62	100
Quantum yield ^a	0.57	0.73	0.78	0.64	0.38
EM ^b (toluene, nm)	437	393	410	400	412
EM ^b (solid, nm)	497	445	413	439	446

^a Relative to Rhodamine B in toluene.

^b EM = emission maximum.

almost unchanged after 10 h and that the *trans* structure was photostable.

Fluorescence Spectra

The fluorescence spectra of TPA polymers in solution is shown in Figure 6. The emission maximum of copolymer **III** was 417 nm in dimethyl sulfoxide (DMSO; excited at 352 nm) and 410 nm in toluene (excited at 354 nm), whereas the intensity in toluene was much higher than that in DMSO solution. PTPA had a violet emission with a maximum at 412 nm in toluene.

Figure 7 shows the fluorescence spectra of copolymer **III** in toluene solution. The emission intensity decreased with decreasing concentration; no concentration quenching or excimer was observed in this condition.

The quantum yields of the copolymers in solution are shown in Table III, which were generally

positively related to the content of TPA moieties in the polymers. However, PTPA had much lower yields than the copolymers.

The photoluminescent (PL) spectra of the solid-state film of the polymers spin-coated on SiO₂ glass are shown in Figure 8, and the emission maxima are listed in Table III. The homopolymeric TPA showed a blue light emission, illustrating that it could also contribute luminescence to the LED.

The solid-state PL of the copolymers were quite different from each other. From copolymer **I** to copolymer **III**, the emission shifted from yellow to blue then to the violet region while the emitting band became narrower. The narrow bandwidth emitting from solid-state film was determined reproducibly not only from Polymer IV but also from the carbazole–stilbene copolymer.¹⁰ The emission maximum was negatively related to the TPA unit

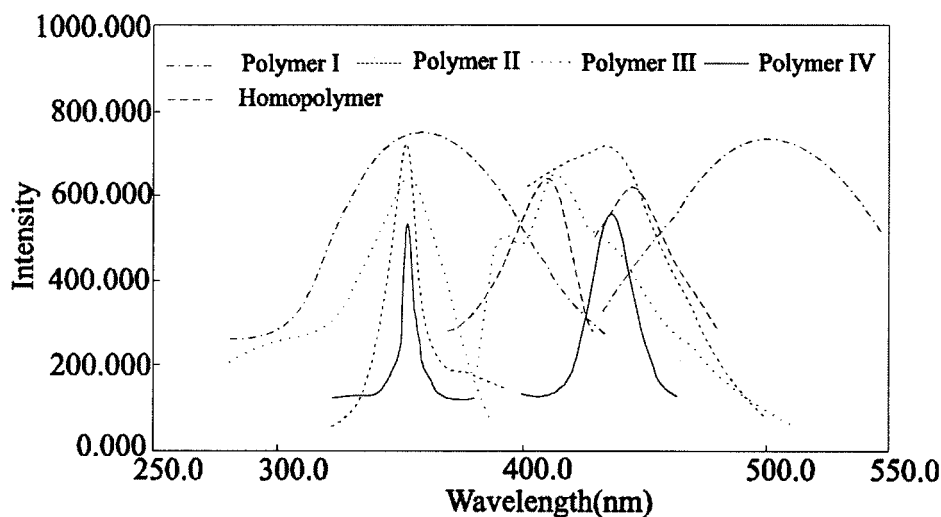


Figure 8 Fluorescence spectra of the solid membrane of TPA-containing polymers (slit width = 3 nm).

content (Table III). However, copolymer IV offered pure blue emission, which may have been due to its higher molecular weight (higher inherent viscosity in Table I) and proper TPA content.

CONCLUSIONS

1. Oxidative-coupling polymerization is a facile method used to prepare polymeric TPA.
2. TPA–stilbene copolymers have a higher solubility than homopolymeric TPA.
3. The TPA homopolymer exhibits photoluminescent properties, whereas the TPA–stilbene copolymers have higher quantum yields than the homopolymer.
4. In the solid-state film, the homopolymeric TPA offers blue light emission; the TPA–stilbene copolymers emit light from violet to yellow. Pure blue light emission can be obtained through optimization of the structure of the copolymer.

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