Synthesis and Fluorescence of Copolymer of Triphenylamine and *trans*-Stilbene from Oxidative-Coupling Reaction

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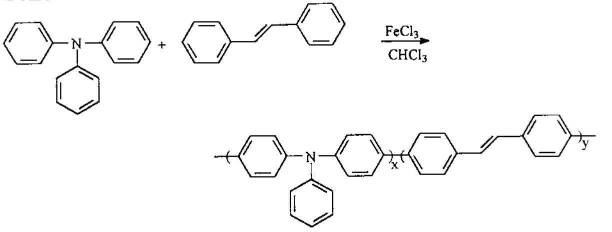
A conjugated polymer was prepared by an oxidation-coupling polymerization of triphenylamine (TPA) and *trans*-stilbene. The structure of the copolymer was characterized by elemental analysis, ^{1}H NMR, UV–vis and FT-IR spectra. The copolymer has good solubility in common organic solvents and high glass transition temperature. Fluorescence spectra showed that the copolymer is violet-blue light emitting material.

Triphenylamine (TPA) and its derivatives have been extensively used as an excellent hole transporting layer (HTL) in fabricating organic electroluminescent (EL) devices,[1] which have great potential use in full color flat panel displays, as a result of their low drive voltage, high efficiency, and high brightness. However, the morphological change of vapor-deposited TPA and its derivatives resulted from operation heat, molecular migration, and promoted by the molecular motion near glass transition temperature (T_g), degrades the EL devices then shortens its life time. Therefore, high T_g and high molecular weight of HTL materials are required for the EL devices. Polymers have another advantage of the processibility, which are fabricated just by spin coating from solution. So that incorporation of TPA in oligomer or polymer main chain is a useful strategy. Tanaka et al. prepared TPA oligomers through an Ulman reaction and fabricated EL devices using the oligomers for the hole-transporting layer, from which an initial luminance exceeding 11000 cd·m^{-2} at 14 V and an operation time over 100 h without serious degradation were observed.[2] Marks et al. fabricated LED devices using crossing-1inked TPA as HTL and obtained a forward light output of 1500 cd·m^{-2} from the device.[3] Many authors reported TPA copolymer used as emitting materials in LED.[4–6] The copolymer of TPA and bisquinoline obtained from Buchward coupling possesses excellent thermal stability and good electron injecting/transporting ability.[4] The copolymers with TPA in PPV backbone prepared by Wittig–Hornor reaction have excellent solubility and high EL efficiency as emitting layer in LED.[5] However, to prepare polymeric TPA, tedious synthetic procedure is necessary. In this article, we present a novel, facile synthetie method to prepare TPA–stilbene copolymer, which contains TPA moieties and double carbon–carbon bonds in the main chain. The synthesis was carried out simply by the oxidative-coupling polymerization of TPA and *trans*-stilbene, without introducing functional groups to the monomers. Therefore, we can expect the copolymer will have good luminescence and charge transporting properties. The synthetic route is shown in Scheme 1. The synthesis, characterization, solubility, absorption and fluorescence spectra were investigated.

Scheme 1.



In a 2-neck flask equipped with gas inlet, electro-magnetic stirrer and funnel, 0.98 g (6 mmol) $FeC1_3$ and 30 mL chloroform were stirred while 0.5 g (2 mmol) TPA and 0.18 g (1 mmol) stilbene were added under argon atmosphere. The reaction was continued overnight at room temperature. Then $FeC1_3$ was filtered off and the filtrate was poured into methanol. The precipitated product was collected by filtration, washed with methanol for several times and dried in an oven at 60 °C. The product was extracted with methanol in Soxhlet's extractor for 2 days to remove the monomers and low molecular weight oligomers. The weight of recovered polymer was 0.33 g, yield 56.9%. Elemental analysis: C, 82.8; H, 4.9.; N, 4.2. The TPA moiety in the copolymer is 74%. The MW measured by GPC against polystyrene standards was 8000. In our experiments the composition of the copolymers varied with the change of the feed ratio of the monomer and polymerization conditions. The contents of the TPA moieties are in the range of 43% to 74% in these copolymers. Although a series polymers with different composition were prepared, but all following data of characterization and properties are obtained from the polymer prepared in above example.

The ^{1}H NMR of the polymer shows triplets at δ 7.59, 7.57 and 7.53 ppm; 7.33, 7.30 and 7.28 ppm; and quaternary signal at 7.05, 7.02, 7.00 and 6.98 ppm, which are tentatively assigned to the mono- and para-linked benzene of TPA and para-linked stilbene moieties respectively.

DSC measurement shows that the copolymer has glass temperature of 220 °C, and TGA determination shows its temperature of decomposition is 300 °C.

FT-IR spectrum exhibits C–H stretch of unsaturated –C=C– bands at 3030 and 3060 cm^{-1}, saturated N–C stretching at 1320 cm^{-1}, unsaturated –C=C– bands at 1600 and 1500 cm^{-1}. The peaks of 700, 750, and 820 cm^{-1} are attributed to mono- and 1, 4-disubstitution of the benzene rings. A weak but sharp band at 960 cm^{-1}, corresponding to the out-of-plane-bending mode of the *trans*-vinylene groups, appeared for the copolymer. Exposing on 365 nm UV light for 10 h, the band does not change obviously. It means that the *cis–trans* isomerization of stilbene moiety does not take place in the copolymer.

The solubility of the copolymer measured at room temperature is shown in Table 1. The results illustrate that the copolymer has good solubility in toluene and tetrachlorocarbon.

Table 1. Solubility of the copolymer (g/100 mL)

Solvent	Toluene	CCl_4	Acetone	DMSO	Alcohol
solubility	1.41	1.61	0.33	0.59	0.09

UV–vis spectrum of the copolymer shows maximum absorption band at 352 nm (ε, 16000) with a shoulder at 315 nm in toluene. For the monomers there only is one band at 300 nm for stilbene and at 296 nm for TPA. The absorption of copolymer relative to two monomers has a great red shift because of polymerization.

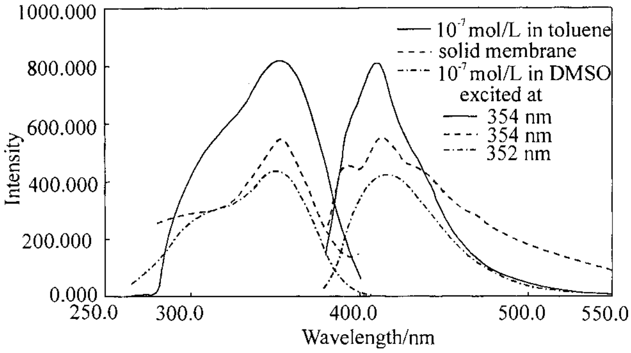


Figure 1. Fluorescence and excitation spectra of the copolymer in solution and solid membrane. (the slit width is 3 nm)

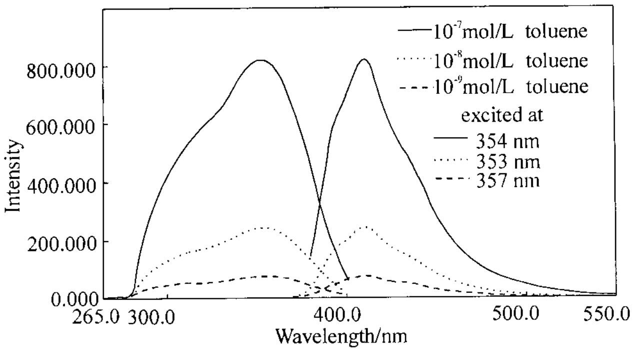


Figure 2. Fluorescence and excitation spectra of the copolymer in toluene. (the slit width is 3 nm)

Figure 1 shows the fluorescence spectra of the copolymer. The photoluminescence (PL) emitting wavelength is 417 nm in DMSO (excited at 352 nm) and 410 nm in toluene (excited at 354 nm) respectively. The polymer had much higher emission intensity in toluene than in DMSO. In the fluorescence spectrum of solid state film of the copolymer spin coated on SiO_2 glass, the maximum emitting wavelength was at 413 nm with a shoulder at 439 nm (excited at 354 nm), affording a blue-violet light emitting. The quantum yield of the copolymers in toluene is from 0.57 to 0.78 relative to Rhodamine B and the emitting wavelength varied from 393 to 437 nm depending on the TPA content. Figure 2 shows the fluorescence spectra of the polymer in toluene, whose intensity decreases quickly with decreasing concentration, but the exciting and emitting wavelength are still unchanged.

In conclusion, a novel kind of copolymers of TPA–stilbene is prepared by a facile oxidative-coupling polymerization. The copolymers exhibit high glass transition temperature, excellent thermal stability, high quantum yield in solution and blue-violet emitting in solid state film.

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