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Poly(4-vinyltriphenylamine): synthesis and application as a hole transport layer in light-emitting diodes

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Summary

An efficient synthesis of 4-vinyltriphenylamine has been developed. This monomer has been polymerised using both anionic and free radical initiators to provide polymers suitable for casting films from solution. Light emitting diodes have been fabricated using this polymer as a hole transport layer (HTL). Comparable devices have been fabricated using evaporated triphenylamine or N,N'-diphenyl-N,N'-ditolylbenzidine as the HTL. Devices with the polymeric HTL display a greater brightness than those with the evaporated layers.

Introduction

We have been prompted by a footnote in recent paper by Bellman *et al* (1) to publish our work on a closely related system. Organic LEDs offer the potential for large area displays (2). Tertiary aromatic amines are probably the most commonly used organic hole transport materials (3). However, vapour deposition techniques are costly and crystallisation in films of organic materials can result in poor performance. Polymeric materials (4) have the advantage that films can be formed by casting from solution and generally such films are less susceptible to the problems of crystallisation.

Here we report the synthesis of poly(4-vinyltriphenylamine) (PVTPA), a polymer with pendant triphenylamine groups on a hydrocarbon backbone, and the fabrication of LEDs using this material as a hole transport layer (HTL). 4-Vinyltriphenylamine was synthesised and polymerised by anionic and free radical procedures (Figure 1). This polymer has been reported previously, however only low yields were obtained by free radical polymerisation (5). This polymer has been chosen to minimise the content of non-conducting polymer backbone.

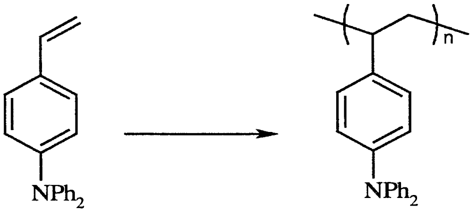


Figure 1 *Poly(4-vinyltriphenylamine)*

Light emitting diodes have been formed using a layer of this polymer as a HTL in the form of a film cast from solution onto ITO coated glass. A second layer consisting of a mixture of isomers (6) of a perinone dye 10/11-methoxy-7-H-benzimidazo[2,1-a]benz[de]isoquinolin-7-one (Figure 2) was deposited on top of the HTL by evaporation and acts as both an electron transport material and luminescent layer.

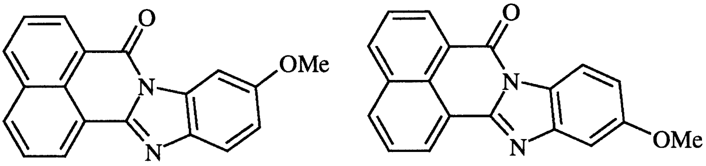


Figure 2 *Perinone dye mixture used in LEDs*

These devices have been compared to similar devices using evaporated layers of either triphenylamine (TPA) or N,N'-diphenyl-N,N'-ditolylbenzidine (TPD) as the HTL. Surprisingly, LEDs constructed with PVTPA HTL gave far brighter devices than those using either TPA or TPD, and gave external quantum efficiencies >1%.

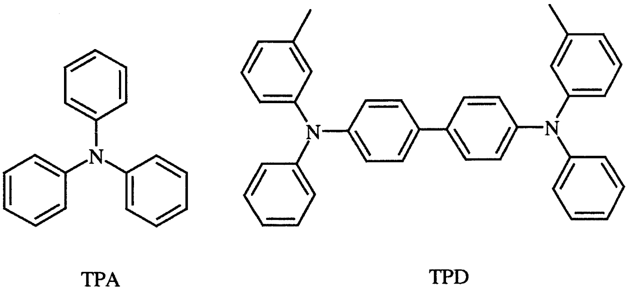


Figure 3 *Comparison compounds used as hole transport layers in this study*

Experimental

Benzene used for polymerisation experiments was washed with concentrated sulphuric acid then aqueous $NaHCO_3$ and dried first by Dean-Stark distillation and further by stirring over CaH_2 for 7 days. It was degassed by repeated freeze-thaw cycles. Other chemicals were purchased and used as received without further purification.

Synthesis of 4-vinyltriphenylamine

4-Acyltriphenylamine was synthesised from acetyl chloride and triphenylamine employing anhydrous zinc chloride as a catalyst according to a previously published procedure (7). 4-Acyl-triphenylamine (31.6g, 0.110 mol) and $Al(O^iPr)_3$ (44.5g, 0.220 mol) were suspended in xylene (100 ml) and refluxed for 3 hours with a flow of nitrogen to remove acetone produced during the reaction. The solution was cooled and poured into water producing a white precipitate of aluminium salts which were removed by filtration. The layers were separated and the aqueous layer extracted with diethyl ether. The organic layers were combined, dried over $MgSO_4$ and the solvent was removed *in vacuo* to give a yellow solid. This was purified by recrystallisation from hexane cooled to -78ºC to yield 4-vinyltriphenylamine as a white solid, (m.pt 87.5 - 89.0ºC, no literature value available) 15.3g, 51%. Found: C, 88.43; H, 6.39; N, 5.16%; $C_{20}H_{17}N$ requires: C, 88.52; H, 6.32, N 5.10%. ^1H NMR (200 MHz, $CDCl_3$) δ 7.4 - 6.8 (m, 20H, aromatic $C\underline{H}$), 6.67 (d of d, $^3J_{HH}$ 10.8 and 17.58 Hz, $ArC\underline{H}CH_2$), 5.65 (d, $^3J_{HH}$ 17.58 Hz, $ArCHC\underline{H}_2$ (trans)), 5.17 (d, $^3J_{HH}$ 10.9 Hz, $ArCHC\underline{H}_2$ (cis)).

Prior to polymerisation the monomer was purified by column chromatography on silica with hexane as an eluent.

Alternative synthesis of 4-vinyltriphenylamine

4-Bromotriphenylamine was synthesised from triphenylamine and N-bromosuccinimide according to a previously published procedure (8). 4-Bromotriphenylamine (5.0g, 15.4 mmol) was refluxed in THF with excess magnesium for 2 hours to form the corresponding Grignard reagent. The solution was filtered (no. 2 sinter) under nitrogen and (dppe)$NiCl_2$ (0.08g, 0.15 mmol) was added to form a brown solution. Vinyl bromide (17 mmol, 1.0M in THF) was added dropwise over 30 mins and the solution stirred overnight. The reaction mixture was quenched with dilute HCl, washed with water, dried over $MgSO_4$ and evaporated to give a pale green solid which was purified by column chromatography on silica with hexane eluent to yield 4-vinyltriphenylamine as a white solid (3.1g, 74%).

Anionic polymerisation of 4-vinyltriphenylamine

Prior to polymerisation, 4-vinyltriphenylamine was dissolved in hexane and stirred over calcium hydride overnight. After filtration (cannular filter) the solution was cooled to -20°C upon which 4-vinyltriphenylamine crystallised. This solid was recovered by filtration and dried under high vacuum (10^{-6} mbar), after which the material was handled under dry nitrogen and never exposed to the atmosphere.

In a typical polymerisation benzene (60 ml) was condensed onto 4-vinyltriphenylamine (1.50g, 5.5 mmol) in an ampoule under vacuum and ^sBuLi (32.5 µmol, 1.3M solution in cyclohexane) added via a septum using a syringe. A deep orange colour formed immediately and the solution was stirred for 24 hours. The polymerisation was terminated by the addition of a small quantity of methanol giving a colourless solution. The polymer was precipitated by pouring the solution into an excess of methanol. The polymer was recovered by filtration and dried under vacuum to yield 1.2g of a white powder.

GPC analysis (Waters system, differential refractometer detector, three PL-gel columns (exclusion limits 10, 10^3 and 10^5Å), calibrated using polystrene standards (Polymer Labs), $CHCl_3$ solvent) gave $\overline{M_n}$ 9500, $\overline{M_w}$ 9900, $\overline{M_w} / \overline{M_n}$ 1.03

^1H NMR (300 MHz, $CDCl_3$) δ 6.4 - 7.2 (br, m, 14H, aromatic H), 1.2 - 2.4 (br, m, 3H, aliphatic H)

TGA Data (Stanton Redcroft TG760 thermobalance, heating rate 10°C min^{-1} under nitrogen atmosphere) gave 5% wt loss 390 ± 10°C, 2% wt loss 310 ± 10°C

Differential Scanning Calorimetry (Perkin Elmer Pyris 1 system, Cryofill subambient unit, scan rate 10°C / min between -150 and 290 °C, values quoted are from the second run) gave an unassigned endothermic transition -7°C; T_g 146°C

Free radical polymerisation of 4-vinyltriphenylamine

4-Vinyltriphenylamine (0.46g, 17 mmol) and AIBN (7.6 mg, 46 µmol) were placed in an ampoule and benzene (5ml) condensed into the ampoule under vacuum. The solution was then heated in the ampoule to 80°C for 10 hours, cooled and the product poured into methanol (50ml). The polymer which precipitated was collected by filtration and dried under vacuum to yield 0.35g of a white powder.

GPC analysis (as above): $\overline{M_n}$ 5500, $\overline{M_w}$ 9940, $\overline{M_w} / \overline{M_n}$ 1.82

Fabrication and Evaluation of Devices

In order to make a comparison between the newly synthesised material and similar monomer materials, a number of light-emitting diode devices were fabricated. The device geometry is shown in Figure 4. The devices were built on 1.1mm glass substrates. A 30nm thick indium tin oxide (ITO) layer acted as the anode. The TPD and TPA hole transport layers were deposited by thermal evaporation at a base pressure of ~10^{-6} Torr. The films were 85nm thick and deposited at a rate of 3-4Å/s. The PVTPA was readily soluble in dichlorobenzene and was spin deposited out of a 4% solution. The thickness of the PVTPA was varied systematically in order to show the effect of thickness on the device quantum efficiency. For all samples the electron transport and emitting layer was the thermally evaporated perinone dye which was deposited at a thickness of 34nm and a rate of 2-3Å/s. We chose to use an aluminium cathode in this work, both because of its good film deposition properties, and also due to its higher stability in air compared with lower work function cathodes. The aluminium films were typically 100nm thick and were deposited at a rate of ~2Å/s. The aluminium films were deposited through a mask which allowed a number of circular areas to be tested independently. Electrical connections were made to the device by indium soldering to the ITO and by contacting a fine gold wire directly on to the aluminium cathode. All film thicknesses were measured using a Dektak surface profiler and quartz crystal thickness monitor. Devices were evaluated in air using a Keithley 236 Source Measure unit to assess the electrical characteristics and to provide a constant current source for electroluminescence (EL) measurements. EL and photoluminescence (PL) spectra and intensities were measured using a Photo Research SpectraScan 714 spot photometer.

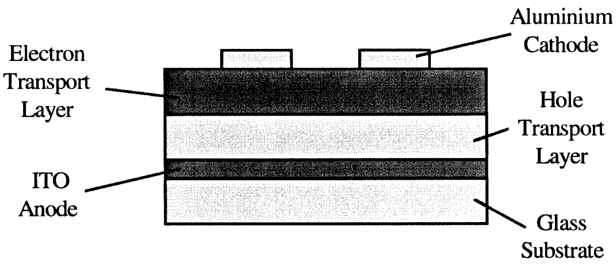


Figure 4 OLED device geometry

Results and discussion

4-Vinyltriphenylamine behaves as a substituted styrene, undergoing living anionic polymerisation despite the presence of an electron donating diphenylamine group in conjugation with the vinyl group which is expected to destabilise the propagating anion. The synthesis gives polymers of narrow polydispersities and molecular weights determined by the ratio of initiator to monomer. The monomer also undergoes free radical polymerisation to give soluble polymers with molecular weight distribution ($\overline{M_w} / \overline{M_n}$ 1.9) consistent with a well-behaved radical polymerisation.

The polymer shows a high thermal stability experiencing only a 5% weight loss up 390°C. DSC measurements indicate a T_g of 146°C. Another transition occurs at -7°C which may be associated with motion of the pendant triphenylamine groups. Similar transitions are seen in triphenylamine intself. There is no evidence of crystallinity in the polymer.

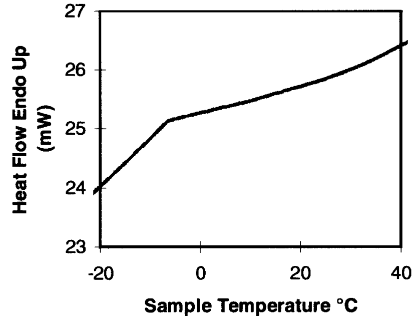


Figure 5 Selected region of DSC trace of poly(4-vinyltriphenylamine)

Organic LED devices made with an evaporated TPA layer showed poor performance, consistent with a high trap density in the microcrystalline hole transport layer. Many of the devices contained short circuit defects; functional devices showed good diode behaviour with a rectification ratio of ca. 230:1 at 14V, but the current carrying capacity was low. Under forward bias, light emission could be observed. At a current density of 40mA/cm^2 the luminance level was 1.2cd/m^2 corresponding to a low external quantum efficiency of ca. 1.3 x 10^{-3} %.

Devices made with PVTPA as the HTL performed better by orders of magnitude. Figure 6 shows the current/voltage (I/V) characteristics for four devices made using different PVTPA thicknesses. The results show strong rectification, with threshold voltages for light emission of between 5 and 10V. Figure 7 shows the variation of luminance with current density for the various devices. A peak brightness of 2500 cd/m^2 was observed in these devices. The quantum efficiency of the devices was calculated from the current/luminance data (assuming Lambertian emission), and at 100mA/cm^2 varied between 0.45 and 1.05% depending on the HTL thickness.

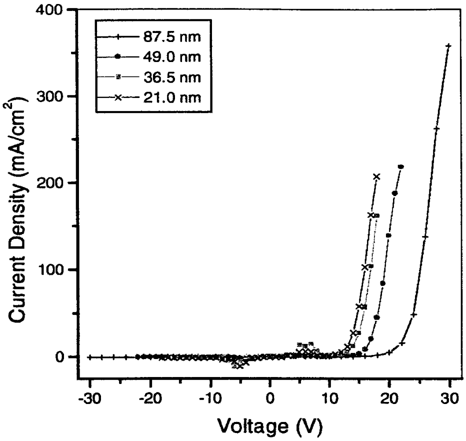


Figure 6 Current/Voltage characteristic Of PVTPA/ Perinone devices. HTL thicknesses 21-87.5nm.

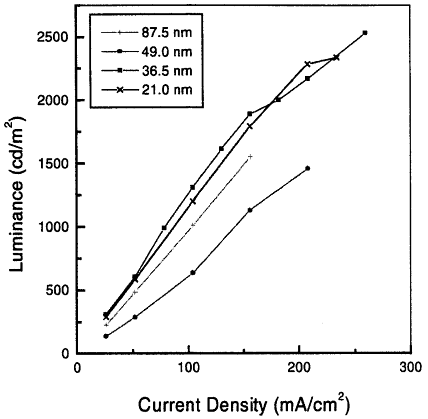


Figure 7 Variation of current with luminance for the PVTPA/Perinone devices.

Since the species responsible for charge transport is similar in both TPA and PVTPA materials, it seems likely that it is the physical structure of the polymer that enhances its charge transport properties as compared with the monomer. Attaching the carrier units to a polymer results in a disordered arrangement and avoids the problems of phase segregation which can occur in solid solutions of organic hole transport materials in polymer matrices. The use of side-chain polymers to overcome such problems has proved successful in other systems (9). This approach allows us to use the minimum quantity of inert polymer material to stabilise the film hence minimising the effect on the hole mobility of the material.

TPD and its derivatives are a popular choice for HTL fabrication in devices. TPD is subject to crystallisation but the process is considerably slower than in TPA and for the duration of the experiment, the film was essentially amorphous. TPD also has a lower energy barrier to hole injection from an ITO electrode, and a higher hole mobility than TPA (10, 11). Hence one might expect the evaporated TPD devices to be more efficient than the PVTPA polymer LEDs. The I/V characteristic for the TPD device shown in Figure 8 demonstrates the superior electrical characteristics of the TPD device over a similar thickness of PVTPA. The TPD device shows a lower threshold for light emission ~4V compared with ~10V for the polymer film. In addition the TPD device shows a much higher current carrying capability before breakdown; the mechanism for electrical breakdown in each case being destruction of the Al cathode which indicates that injection of electrons is the limiting constraint in both devices.

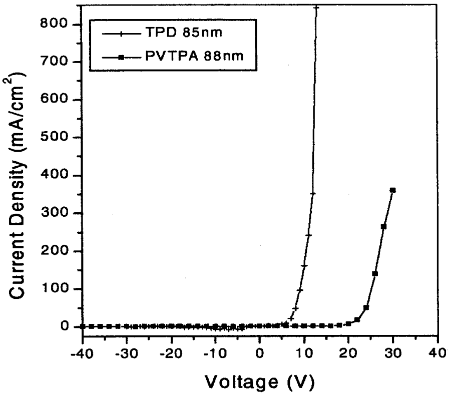


Figure 8 Comparison of the I/V characteristics for equivalent devices made from PVTPA and TPD.

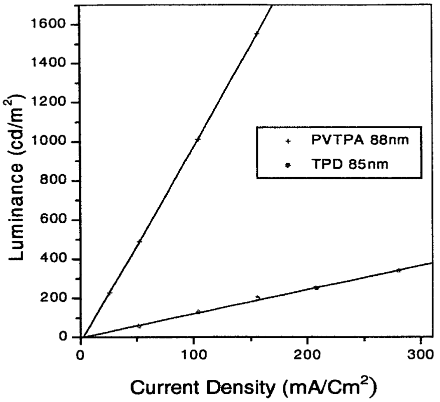
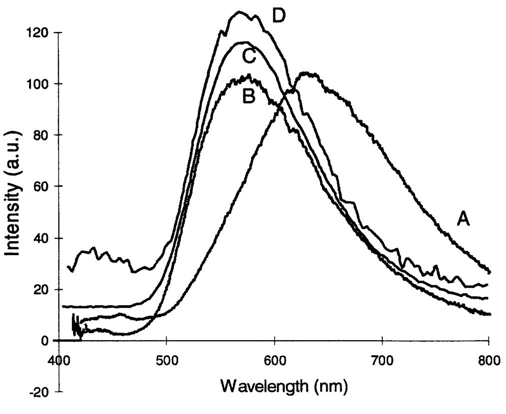


Figure 9 Comparison of the variation of luminance with current for equivalent devices made from PVTPA and TPD.

Perhaps surprisingly the light output from the TPD device is considerably lower than for the PVTPA device. Figure 9 shows a comparison of the two equivalent devices – the PVTPA is clearly superior. The explanation for this becomes clear on observing the PL and EL spectra for both materials (Figure 10). For the PVTPA device the EL and PL emission overlay exactly and correspond closely to the emission seen from a film of the perinone dye alone. However in the case of the TPD device, there is a distinct redshift (40nm) of the EL relative to the PL. Whilst the PL is generated throughout the bulk of the emitting layer; the EL arises at the junction between the ETL and HTL, and decays exponentially into the perinone layer. This redshift between the spectra tells us that the local emission environment at the interface has been modified, possibly by formation of an exciplex. Although there is evidence in the



A) TPD/perinone device, EL spectrum

B) TPD/perinone device, PL spectrum

C) PVTPA/perinone device, EL spectrum

D) PVTPA/perinone device, PL spectrum

The emission spectrum of the perinone dye is essentially identical to that of traces B, C, D. PVTPA has no strong emission in the visible.

Figure 10 Normalised emission spectra of devices described in this paper.

literature (12) which suggests that the redshift associated with an exciplex can be useful in colour-tuning OLED devices; in this case it would seem that the exciplex has a fast non-radiative decay route which reduces the overall quantum efficiency to ca. 0.15% at 100mA/cm^2. Devices made using an evaporated TPA layer show two overlapping EL emission maxima of similar intensity which correspond to the perinone and to an exciplex peak.

Conclusion

We have developed an efficient synthesis of 4-vinyltriphenylamine. This monomer has been polymerised anionically in a living manner to give well-defined polymers suitable for casting films from solution. This polymer has been used as a hole transport material in the fabrication of LEDs. These devices proved to be far brighter than comparable devices made with either TPA or TPD. In the case of the TPA, we attribute this to organisation of carrier sites attached to the polymer backbone which inhibits crystallisation of the triphenylamine units. In the case of the TPD HTL, exciplex formation at the light emitting interface is likely to be responsible for the loss of efficiency in the device performance.

References

1. Footnote 44, Bellmann E, Shaheen SE, Thayumanavan S, Barlow S, Grubbs RH, Marder SR, Kippelen B, Peyghambarian N (1998) Chem. Mater. 10:1668.

2 Dodabalapur A (1997) Solid State Commun. 102:259

3 Bellmann E, Shaheen SE, Thayumanavan S, Barlow S, Grubbs RH, Marder SR, Kippelen B, Peyghambarian N (1998) Chem. Mater. 10:1668 and references therein give access to the literature of this area.

4 Kraft A, Grimsdale AC, Holmes AB (1998) Angew. Chem. Int. Ed. Eng 37:402.

5 Compton RG, Laing ME, Ledwith A, Abuabdoun II (1988) J. Appl. Electrochem. 18:431

6 Grayshan PH and Peters AT (1973) J. Heterocyclic Chem. 10:705.

7 Fox CJ and Johnson AL (1964) J. Org. Chem. 29:3536.

8 Creason SC (1972), J. Org. Chem. 49:4440.

9 Examples include Boyd TJ, Geerts Y, Lee J-K, Fogg DE, Lavoie GG, Schrock RR, Rubner MF, (1997) Macromol. 30:3553; Kolb ES, Gaudiana RA, Mehta PG (1996) Macromol. 29:2359.

10 Stolka M, Yanus JF and Pai DM (1984) J. Phys. Chem. 88:4707.

11 Pfister G (1977) Phys. Rev. B 16:3676.

12 Itano K, Ogawa H and Shirota Y (1998) Appl. Phys. Lett. 65:807.