

New Triarylamine-Containing Polymers as Hole Transport Materials in Organic Light-Emitting Diodes: Effect of Polymer Structure and Cross-Linking on Device Characteristics

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A series of poly(norbornenes) with pendant triarylamine (TPA) groups has been synthesized by ring-opening metathesis polymerization and investigated as hole transport materials in organic two-layer light-emitting diodes (LEDs). Efficient device fabrication through spin casting of the hole transport layer (HTL) was possible, since the polymers exhibited excellent film formation properties. LEDs of the form ITO/poly(norbornene)-TPA/Alq₃/Mg (ITO = indium tin oxide, Alq₃ = tris(8-quinolinato)aluminum) showed bright green emission with external quantum efficiencies of up to 0.77% (1.30 lm/W) for 20 nm thick HTL films. The length and polarity of the linker between the triarylamine functionality and the polymer backbone were varied systematically. The device performance was found to depend strongly on these structural differences. Substitution of ester groups by less polar ether functionalities greatly enhances external quantum efficiencies, lowers the operating voltage, and improves the stability of the device. Further improvement of the device characteristics is achieved by reducing the length of the alkyl linker. The HTL can be conveniently cross-linked by UV irradiation. Cross-linking was found to decrease device performance. A maximum external quantum efficiency of 0.37% was achieved for an Alq₃-LED with cross-linked HTL.

Introduction

Organic hole transport materials find applications in organic light-emitting diodes (LEDs), where they substantially increase device performance if placed as a hole transport layer (HTL) between the anode and the luminescent layer. An organic material is a potential hole transporter if it can reversibly form radical cations, e.g., if it can accept and donate positive charges without decomposition. The triarylamine functionality is known to fulfill this requirement and constitutes a key feature of many organic hole transport materials.¹

Figure 1 shows the structures of two widely studied triarylaminines. Their hole transport properties have been investigated,^{2–6} and they have been used in organic

LEDs.^{1,7–20} Triarylamine-based HTLs are most commonly prepared by vapor deposition of the molecular material.^{1,7–14} Polymeric host–guest systems^{1,15} and covalent incorporation of triarylamine into polymers^{16–20} have also been reported.

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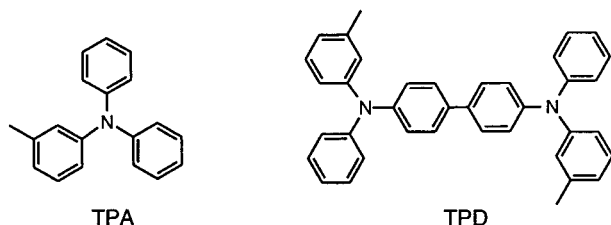


Figure 1. Structures of commonly used organic hole transport materials.

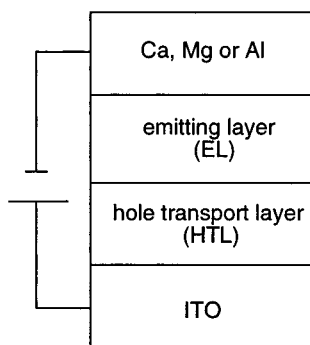


Figure 2. Typical structure of a two-layer LED.

These previous studies showed that physical properties of the systems such as glass transition temperature (T_g), crystallization, phase separation, or structure of the polymeric host are as crucial for the device performance as the favorable reversible oxidation potential of triarylamine. This motivated us to synthesize a series of analogous triarylamine-containing polymers with systematic variations in T_g , linker length, and linker polarity and to study the effect of these structural differences on the performance of two-layer LED devices (Figure 2).

The synthesis and investigation of new hole-transporting polymers is of particular interest, since device fabrication through spin casting of a polymer offers a desirable alternative to vacuum vapor deposition of a molecular material. Large-area and flexible LEDs can be fabricated using polymer films.²¹ Furthermore, covalent incorporation of the hole-conducting moiety onto the polymer chain prevents phase separation, a problem seen in many host-guest systems.¹ Another challenge is the development of cross-linkable hole-transporting polymers. If the hole-transporting polymer remains soluble, the emissive layer (EL) must be vapor deposited to prevent destruction of the first layer through exposure to solvents. Making the HTL insoluble by cross-linking would allow spin casting of a luminescent polymer, thereby further enabling flexibility in device fabrication.

Herein, we report the synthesis of a series of cross-linkable triarylamine-containing poly(norbornenes) by ring-opening metathesis polymerization (ROMP)^{22,23} and their application in organic LEDs. ROMP allows one to convert a large number of substituted cyclic olefins to the corresponding macromolecules under mild conditions^{24–32} providing a variety of comparable polymers (Figure 3). Initiator **1** (Figure 3) has been shown

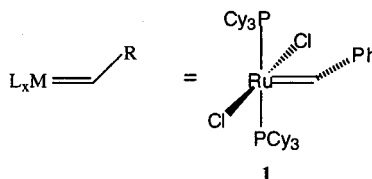
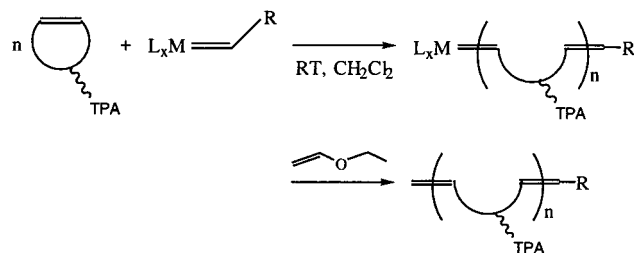


Figure 3. Schematic representation of ring-opening metathesis polymerization (ROMP).

to be remarkably tolerant toward functional groups^{33,34} and to yield living polymerization in many cases.^{24,25}

Experimental Section

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4-Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300 MHz for ¹H; 75 MHz for ¹³C) spectrometer. Gel-permeation chromatograms were obtained on a HPLC system using an Altex model 110A pump, a Rheodyne model 7125 injector with a 100-μL injection loop, American Polymer Standards 10-μm mixed-bed columns, a Knauer differential refractometer, and CH₂Cl₂ as eluent at a 1.0 mL/min flow rate. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 with a scan rate of 10 °C/min. High-resolution mass spectra were provided by the Southern California Mass Spectrometry Facility (University of California at Riverside). Elemental analysis was performed by Midwest Microlabs.

Materials. Methylene chloride used in polymerization experiments was distilled from CaH₂ and degassed by freeze-pumping the liquid several times. Toluene and tetrahydrofuran were distilled from Na/benzophenone. All other reagents and starting materials were purchased from Aldrich Chemical Co. and used as received unless otherwise noted.

Preparation of 1-Bromo-4-(*m*-tolylphenylamino)benzene (2). Tris(dibenzylideneacetone)dipalladium(0) (Pd₂dba₃) (4.00 g, 4.37 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (3.63 g, 6.55 mmol), and 1,4-dibromobenzene (206 g, 873 mmol) were dissolved in 400 mL of dry toluene and stirred for 15 min. Sodium *tert*-butoxide (41.9 g, 436 mmol) and *m*-tolylphenylamine (50 mL, 290 mmol) were then added. The reaction mixture was warmed to 90 °C for 16 h. Thereafter, the reaction mixture was poured into water (1 L) and ether (500 mL), and the aqueous layer was extracted with ether. The

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combined organics were dried over MgSO_4 , and the solvent was evaporated under reduced pressure. Column chromatography (silica, hexanes) afforded 63.4 g (64%) of product **2**. ^1H NMR (CDCl_3) δ 7.33–7.23 (m, 4H), 7.15 (t, 1H, $J = 7.7$ Hz), 7.08–6.86 (m, 8H), 2.27 (s, 3H). ^{13}C NMR (CDCl_3) δ 147.5, 147.3, 147.1, 139.3, 132.1, 129.3, 129.2, 125.2, 125.0, 124.3, 124.2, 123.0, 121.8, 114.6, 21.4. HRMS calcd for $\text{C}_{19}\text{H}_{16}\text{BrN}$ [M^+]: 339.0446. Found: 339.0452. Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{BrN}$: C, 67.47; H, 4.77; N, 4.14. Found: C, 67.42; H, 4.71; N, 4.18.

Preparation of 1-(Hex-5-enyl)-4-(*m*-tolylphenylamino)benzene (3). Compound **2** (12 g, 35 mmol) was dissolved in 500 mL of THF and treated with 2 equiv of *tert*-BuLi (1.66 M solution in hexanes, 45 mL) at -78°C under an inert gas atmosphere. 6-Bromohexene (14.5 g, 89 mmol) was added, and the solution was allowed to slowly warm to room temperature. After 5 h, water was added to the reaction mixture. The mixture was extracted with ether. After the organic phase was dried over MgSO_4 , the solvent and excess 6-bromohexene were removed under reduced pressure, yielding 11.4 g (94%) of colorless oil. ^1H NMR (CD_2Cl_2) δ 7.3–6.8 (m, 13H), 5.85 (m, 1H), 5.00 (m, 2H), 2.58 (t, 2H, $J = 7.7$ Hz), 2.25 (s, 3H), 2.12 (m, 2H), 1.65 (m, 2H), 1.47 (m, 2H). ^{13}C NMR (CD_2Cl_2) δ 147.9, 147.7, 145.2, 138.8, 138.7, 137.2, 128.8, 128.7, 128.6, 124.3, 124.2, 123.2, 123.0, 121.8, 120.8, 113.8, 34.8, 33.3, 30.7, 28.3, 20.8. HRMS calcd for $\text{C}_{25}\text{H}_{27}\text{N}$ [M^+]: 341.2139. Found: 341.2143. Anal. Calcd for $\text{C}_{25}\text{H}_{27}\text{N}$: C, 87.93; H, 7.97; N, 4.10. Found: C, 87.85; H, 7.89; N, 3.97.

Preparation of 1-(6-Hydroxyhexyl)-4-(*m*-tolylphenylamino)benzene (4). Compound **3** (11.4 g, 33.3 mmol) was placed into a 500-mL flask, and 150 mL of a 0.5 M solution of 9-borabicyclo[3.3.1]nonane (9-BBN) in THF was added under an inert gas atmosphere. The reaction mixture was stirred at room temperature for 24 h and cooled to 0°C . NaOH (26 mL, 3 M) and 22 mL of H_2O_2 solution (30%) were added slowly. The reaction mixture was warmed to 50°C and kept at 50°C for 2 h. The aqueous phase was extracted with ether, and the product was purified by column chromatography (silica, 30% ethyl acetate in hexanes). Yield: 8.8 g, 74%. ^1H NMR (CD_2Cl_2) δ 7.3–6.8 (m, 13H), 3.60 (t, 2H, $J = 6.5$ Hz), 2.58 (t, 2H, $J = 7.7$ Hz), 2.25 (s, 3H), 1.7–1.5 (m, 4H), 1.5–1.3 (m, 4H). ^{13}C NMR (CD_2Cl_2) δ 147.9, 147.7, 145.2, 139.1, 137.8, 128.8, 128.7, 128.6, 124.3, 124.2, 123.5, 123.4, 121.8, 120.8, 62.8, 35.3, 32.8, 31.6, 29.2, 25.7, 20.8. HRMS calcd for $\text{C}_{25}\text{H}_{29}\text{NO}$ [M^+]: 360.2318. Found: 360.2327.

Preparation of 1-(2-Hydroxyethyl)-4-(*m*-tolylphenylamino)benzene (5). 4-Bromophenethanol was protected with a triphenylmethyl (trityl) group by stirring a solution of 4-bromophenethanol (20.3 g, 0.101 mol), trityl chloride (30.97 g, 0.111 mol), and 4-(dimethylamino)pyridine (200 mg) in pyridine (200 mL) under a nitrogen atmosphere at 70°C for 33 h. The protected compound was purified by phase separation between methylene chloride and water and flash column chromatography (silica, 10% ethyl acetate in hexanes). The yield of the trityl-protected 4-bromophenethanol was 74%. The protected 4-bromophenethanol (31.10 g, 70.16 mmol) was coupled to *m*-anisidine (13.3 mL, 77.2 mmol) following the procedure for Pd-catalyzed amination as described for **2**. The reaction time needed was 24 h at 90°C . The reaction mixture was cooled to room temperature and separated between ether and water layers. The combined organic layer was concentrated in vacuo. Column chromatography (silica, 20% methylene chloride in hexanes) afforded a mixture of starting materials and the product. This mixture was dissolved in diethyl ether (150 mL) and treated with 98% formic acid (200 mL). The resultant solution was stirred at room temperature for 90 min. After 90 min, the reaction mixture was separated between ether and water layers, and the ether layer was washed with water and saturated aqueous sodium bicarbonate solution. Concentration of the organic layer and column chromatography (silica, 30% ethyl acetate in hexanes) yielded 9.6 g (45% over 2 steps) of a very viscous material. ^1H NMR (CD_2Cl_2) δ 7.25–6.95 (m, 10H), 6.89 (s, 1H), 6.82 (d, 2H, $J = 7.7$ Hz), 3.81 (q, 2H, $J = 6.3$ Hz), 2.79 (t, 2H, $J = 6.5$ Hz), 2.24 (s, 3H), 1.45 (t, 1H, $J = 5.8$ Hz). ^{13}C NMR (CD_2Cl_2) δ 148.4,

148.2, 146.6, 139.5, 133.6, 130.2, 129.5, 129.4, 125.1, 124.7, 124.1, 123.9, 122.7, 121.6, 63.8, 38.9, 21.5. HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{NO}$ [M^+]: 304.1701. Found: 304.1696.

Preparation of 1-Methoxy-3-(*m*-tolylphenylamino)benzene (6). 3-Bromoanisole was reacted with 1 equiv of *m*-tolylphenylamine in analogy to the procedure described for **2**. The reaction time needed was 8 h at 95°C . The yield after purification (silica gel column, 5% ethyl acetate in hexanes) was 83%. ^1H NMR (CD_2Cl_2) δ 7.3–6.85 (m, 10H), 6.65–6.55 (m, 3H), 3.70 (s, 1H), 2.27 (s, 1H). ^{13}C NMR (CD_2Cl_2) δ 161.1, 149.8, 148.4, 148.2, 139.7, 130.3, 129.7, 129.6, 125.8, 124.8, 124.4, 123.2, 122.3, 116.8, 110.2, 108.3, 55.7, 21.7. HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$ [M^+]: 289.1467. Found: 289.1469. Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.89; H, 6.76; N, 4.66.

Preparation of 1-Hydroxy-3-(*m*-tolylphenylamino)benzene (7). To a solution of **6** (12.8 g, 44.2 mmol) in 200 mL of dry CH_2Cl_2 at -78°C under an inert gas atmosphere was added 13.3 g (53.1 mmol) of BBr_3 . The solution was stirred at -78°C for 5 min and at room temperature for 3 h. Ice-water (150 mL) was added, and the reaction mixture was stirred for another 3 h. Extraction with CH_2Cl_2 followed by column chromatography (silica, 10% ethyl acetate in hexanes) afforded 8.3 g (68%) of **7**. ^1H NMR (CD_2Cl_2) δ 7.3–6.85 (m, 10H), 6.62 (m, 1H), 6.50 (t, 1H, $J = 2.1$ Hz), 6.45 (m, 1H), 5.04 (bd s, 1H), 2.27 (s, 3H); ^{13}C NMR (CD_2Cl_2) δ 156.9, 150.0, 148.3, 148.1, 130.6, 129.8, 129.7, 126.1, 125.1, 124.7, 123.5, 122.6, 116.4, 110.8, 109.8, 21.7. HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{NO}$ [M^+]: 275.1310. Found: 275.1312. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.92; H, 6.21; N, 5.13.

Preparation of the Ester Monomers 8, 9, and 10. To a solution of the respective alcohol **4**, **5**, or **7** in THF were added 1 equiv of norborn-2-ene-5-carbonyl chloride³⁵ and 2 equiv of triethylamine. The reaction mixture was heated to 50°C for 5 h in the case of **8** and **9** or stirred at room temperature for 2 h in the case of **10**. The triethylamine hydrochloride was filtered off, the solvent was removed under reduced pressure, and the products were purified by column chromatography (silica, 5% ethyl acetate in hexanes). Yields: 95–100%.

8 (mixture of endo and exo): ^1H NMR (CD_2Cl_2) δ 7.3–6.8 (m, 13H), 2H: 6.20 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz) + 6.15 (m) + 5.94 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz), 4.04 (m, 2H), 2H: 3.21 (bd s) + 3.04 (bd s) + 2.95 (m), 2.58 (t, 2H, $J = 7.7$ Hz), 2.25 (s and m, 4H), 1.7–1.2 (m, 12H). ^{13}C NMR (CD_2Cl_2) δ 174.5, 147.9, 147.7, 145.2, 139.2, 138.0, 137.7, 135.8, 132.4, 128.8, 128.7, 128.6, 124.3, 124.2, 123.2, 123.0, 121.8, 120.8, 64.5, 64.2, 49.6, 46.7, 46.3, 45.8, 43.3, 43.2, 42.7, 41.7, 35.3, 31.5, 30.3, 29.0, 28.7, 25.9, 20.8. HRMS calcd for $\text{C}_{33}\text{H}_{37}\text{NO}_2$ [M^+]: 480.2899. Found: 480.2902.

9 (mixture of endo and exo): ^1H NMR (CD_2Cl_2) δ 7.3–6.8 (m, 13H), 2H: 6.15 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz and m) + 5.76 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz), 4.23 (m, 2H), 4H: 3.15 (bd s) + 3.0–2.8 (m), 2.25 (s, 3H), 1.9 (m, 1H), 1.5–1.3 (m, 4H). ^{13}C NMR (CD_2Cl_2) δ 174.0, 147.9, 147.7, 146.0, 138.8, 137.7, 137.3, 132.4, 130.7, 128.8, 128.7, 128.6, 124.3, 124.2, 123.2, 123.0, 121.8, 120.8, 64.5, 64.2, 49.3, 46.7, 46.3, 45.5, 43.0, 42.9, 42.3, 41.4, 34.2, 30.0, 30.3, 28.7, 20.8. HRMS calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_2$ [M^+]: 424.2261. Found: 424.2276. Anal. Calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_2$: C, 82.24; H, 6.90; N, 3.31. Found: C, 81.86; H, 6.96; N, 3.32.

10 (mixture of endo and exo): ^1H NMR (CD_2Cl_2) δ 7.3–6.6 (m, 13H), 2H: 6.22 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz) + 6.15 (m) + 5.98 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.7$ Hz), 2H: 3.32 (bd s) + 3.12 (m) + 2.94 (bd s), 2.25 (s, 3H), 1.95 (m, 1H), 1.6–1.2 (m, 4H). ^{13}C NMR (CD_2Cl_2) δ 173.7, 152.2, 149.6, 148.1, 147.9, 139.8, 138.9, 138.8, 136.3, 132.8, 130.2, 129.92, 129.90, 126.1, 125.2, 124.9, 123.7, 122.7, 121.0, 120.9, 116.8, 115.8, 64.5, 64.4, 50.3, 47.4, 47.0, 46.5, 44.2, 43.9, 43.3, 42.4, 29.9, 20.8. HRMS calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2$ [M^+]: 396.1968. Found: 396.1964. Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 82.06; H, 6.51; N, 3.58.

Preparation of 1-(6-Iodoethyl)-4-(*m*-tolylphenylamino)benzene (11). A solution of triphenylphosphine (8.76 g, 33.4 mmol) and imidazole (2.32 g, 33.4 mmol) in acetonitrile/ether (1:3, 80 mL) was cooled to 0 °C, and iodine (8.48 g, 33.4 mmol) was added slowly under vigorous stirring, yielding a yellow slurry. The ice bath was removed, and the reaction mixture was stirred at room temperature for 15 min. A solution of **4** (4 g, 11 mmol) in 20 mL of the acetonitrile/ether solvent mixture was then added dropwise, and the reaction mixture was stirred for 1 h. Filtration through a plug of silica with 5% ethyl acetate in hexanes as eluent afforded 5.07 g (97%) of pure product. ¹H NMR (CD₂Cl₂) δ 7.3–6.8 (m, 13H), 3.22 (t, 2H, *J* = 6.9 Hz), 2.58 (t, 2H, *J* = 7.7 Hz), 2.25 (s, 3H), 1.85 (m, 2H), 1.65 (m, 2H), 1.42 (m, 4H). ¹³C NMR (CD₂Cl₂) δ 147.9, 147.7, 145.2, 139.1, 137.6, 128.8, 128.7, 128.6, 124.3, 124.2, 123.5, 123.4, 121.8, 120.8, 35.2, 33.6, 31.4, 30.4, 28.3, 20.8, 7.6. HRMS calcd for C₂₅H₂₈NI [M⁺]: 469.1279. Found: 469.1267. Anal. Calcd for C₂₅H₂₈NI: C, 63.97; H, 6.01; N, 2.98. Found: C, 63.93; H, 5.96; N, 2.80.

Preparation of 1-(2-Iodoethyl)-4-(*m*-tolylphenylamino)benzene (12). **12** was prepared in analogy to **11** in 97% yield. ¹H NMR (CD₂Cl₂) δ 7.3–6.8 (m, 13H), 3.35 (t, 2H, *J* = 7.2 Hz), 3.12 (t, 2H, *J* = 7.2 Hz), 2.25 (s, 3H). ¹³C NMR (CD₂Cl₂) δ 147.9, 147.7, 146.7, 139.3, 135.0, 129.18, 129.16, 129.0, 125.0, 124.0, 123.8, 122.6, 121.5, 39.8, 20.8, 6.3. HRMS calcd for C₂₁H₂₀NI [MH⁺]: 414.0726. Found: 414.0719. Anal. Calcd for C₂₁H₂₀NI: C, 61.03; H, 4.88; N, 3.39. Found: C, 61.06; H, 4.96; N, 3.28.

Preparation of 1-(6-((Norboren-2-en-5-yl)methoxy)hexyl)-4-(*m*-tolylphenylamino)benzene (13). Norborn-2-ene-5-methanol (0.53 g, 4.3 mmol) was dissolved in 20 mL of THF and treated with NaH (0.15 g, 6.4 mmol) at 0 °C. After stirring for 15 min, a solution of **11** (4 g, 4.3 mmol) in THF (10 mL) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred for 6 h. Water was added, and the reaction mixture was extracted with ether. Removing the solvent under reduced pressure and column chromatography afforded 0.44 g (22%) of the desired product as a mixture of endo and exo isomers. ¹H NMR (CD₂Cl₂) δ 7.3–6.8 (m, 13H), 2H: 6.12 (dd, *J*₁ = 3.0 Hz, *J*₂ = 5.7 Hz) + 6.09 (m) + 5.95 (dd, *J*₁ = 3.0 Hz, *J*₂ = 5.7 Hz), 4H: 3.37 (m) + 3.23 (t, *J* = 7.2 Hz) + 3.13 (dd, *J*₁ = 6.6 Hz, *J*₂ = 9.3 Hz) + 3.00 (t, *J* = 9.0 Hz), 3H: 2.90 (bd s) + 2.79 (bd s) + 2.74 (bd s) + 2.34 (m), 2.58 (t, 2H, *J* = 7.7 Hz), 2.25 (s, 3H), 12H: 1.83 (m) + 1.7–1.5 (m) + 0.51 (m). ¹³C NMR (CD₂Cl₂) δ 147.9, 147.7, 145.2, 138.8, 137.5, 136.7, 136.3, 132.4, 128.8, 128.7, 128.6, 124.3, 124.2, 123.2, 123.0, 121.8, 120.8, 75.1, 74.2, 70.6, 70.4, 49.1, 48.71, 48.57, 44.7, 43.8, 43.5, 42.0, 41.3, 35.0, 33.3, 31.3, 20.1, 29.5, 29.3, 29.0, 28.8, 25.8, 25.0, 20.8, 7.1. HRMS calcd for C₃₃H₃₉NO [M⁺]: 465.3032. Found: 465.3028.

Preparation of 1-((Norboren-2-en-5-yl)methoxy)-3-(*m*-tolylphenylamino)benzene (14). A solution of norborn-2-ene-5-methanol (1.8 g, 14.5 mmol), **7** (4 g, 14.5 mmol), and triphenylphosphine (5.7 g, 22 mmol) in 250 mL of THF was cooled to 0 °C. Diethyl azodicarboxylate (DEAD) (2.53 g, 14.5 mmol) was added dropwise, and the solution was stirred at room temperature for 6 h. After addition of water, the reaction mixture was extracted with ether. Purification by column chromatography (silica, 5% ethyl acetate in hexanes) yielded 2.64 g (48%) of product as a mixture of endo and exo isomers. ¹H NMR (CD₂Cl₂) δ 13H: 7.3–6.85 (m) + 6.75–6.55 (m), 2H: 6.18 (dd, *J*₁ = 3.0 Hz, *J*₂ = 5.7 Hz) + 6.15 (m) + 5.98 (dd, *J*₁ = 3.0 Hz, *J*₂ = 5.7 Hz), 2H: 4.00 (dd, *J*₁ = 6.0 Hz, *J*₂ = 9.3 Hz) + 3.79 (t, *J* = 9.0 Hz) + 3.66 (dd, *J*₁ = 6.3 Hz, *J*₂ = 9.0 Hz) + 3.15 (t, *J* = 9.0 Hz), 7H: 3.05 (bd s) + 2.89 (m) + 2.55 (m) + 1.92 (m) + 1.51 (m) + 1.45–1.2 (m) + 0.63 (m), 2.30 (s, 3H). ¹³C NMR (CD₂Cl₂) δ 160.6, 149.8, 149.7, 148.5, 148.3, 139.6, 138.1, 137.4, 137.1, 133.0, 130.4, 130.3, 129.8, 129.6, 125.8, 124.9, 124.4, 123.2, 122.4, 117.1, 111.2, 111.1, 109.1, 72.8, 72.0, 50.1, 45.7, 44.5, 44.3, 42.9, 42.2, 39.2, 39.0, 30.2, 29.7, 22.1. HRMS calcd for C₂₇H₂₇NO [MH⁺]: 382.2171. Found: 382.2175. Anal. Calcd for C₂₇H₂₇NO: C, 85.00; H, 7.13; N, 3.67. Found: C, 84.78; H, 7.18; N, 3.68.

General Polymerization Procedure. In a nitrogen-filled drybox, a solution of the monomer and a solution of the

initiator **1**³³ in CH₂Cl₂ were prepared (1 mL of solvent was used for every 100 mg of monomer; the initiator was dissolved in a minimum amount of solvent; monomer-to-initiator ratio was 100). The reaction was initiated by adding the initiator solution to the vigorously stirred monomer solution. The reaction mixture was stirred for 2.5 h. Outside the drybox, the reaction was terminated by adding a small amount of ethyl vinyl ether and the mixture was poured into methanol to precipitate the polymer. The polymer was purified by dissolving in CH₂Cl₂ and reprecipitating into methanol several times and drying in vacuo. Isolated yields ranged from 85% to 95% (100% by NMR).

Poly-8: ¹H NMR (CDCl₃) δ 7.3–6.8 (bd m, 13H), 5.6–5.2 (bd, 2H), 4.0 (bd s, 2H), 5H: 3.2 (bd) + 2.9 (bd) + 2.6 (two broad signals overlap), 2.2 (bd, 3H), 12H: 2.0 (bd) + 1.7 (bd) + 1.4 (bd) + 1.2 (bd).

Poly-9: ¹H NMR (CDCl₃) δ 7.3–6.8 (bd m, 13H), 5.6–5.2 (bd, 2H), 4.0 (bd s, 2H), 5H: 3.2 (bd) + 2.9 (two broad signals overlap) + 2.5 (bd), 2.2 (bd, 3H), 4H: 2.0 (bd) + 1.8 (bd) + 1.4 (bd).

Poly-10: ¹H NMR (CDCl₃) δ 7.3–6.6 (bd m, 13H), 5.6–5.2 (bd, 2H), 3.2–2.3 (bd, 3H), 2.2 (bd, 3H), 4H: 2.1–1.6 (bd) + 1.4 (bd).

Poly-13: ¹H NMR (CDCl₃) δ 7.3–6.8 (bd m, 13H), 5.6–5.2 (bd, 2H), 4H: 3.4 (bd) + 3.2 (bd), 3.0–2.4 (bd, 5H), 2.2 (bd, 3H), 12H: 1.9 (bd) + 1.6 (bd) + 1.4 (bd) + 1.2 (bd).

Poly-14: ¹H NMR (CDCl₃) δ 7.3–6.8 (bd m, 13H), 5.6–5.2 (bd, 2H), 2H: 3.8 (bd) + 3.6 (bd), 3.0–2.2 (bd, 3H), 2.2 (bd, 3H), 4H: 2.0–1.5 (bd) + 1.2 (bd).

Fabrication and Characterization of Light-Emitting Devices. Devices were fabricated on ITO-coated glass substrates with a sheet resistance of 20 Ω/sq (Donnelly Corporation) which had been ultrasonicated in acetone and methanol, dried in a stream of nitrogen, and then plasma etched for 60 s. Polymer layers were formed by spin casting from chlorobenzene solutions (10 g/L). The second layer consisted of vacuum vapor deposited Alq₃ (50 nm) which had been purified by recrystallization and sublimation prior to deposition. Mg cathodes (200 nm) were thermally deposited at a rate of 8 Å/s through a shadow mask to create devices 3 × 5 mm in area. Current–voltage and light output characteristics of the devices were measured in forward bias. Device emission was measured using a silicon photodetector at a fixed distance from the sample (12 cm). The response of the detector had been calibrated using several test devices, for which the total power emitted in the forward direction was measured with a NIST traceable integrating sphere (Labsphere). Photometric units (cd/m²) were calculated using the forward output power and the electroluminescence spectra of the devices. Efficiencies were measured in units of external quantum efficiency (% photons/e⁻). Cathode deposition and device characterization were performed in a nitrogen drybox (VAC).

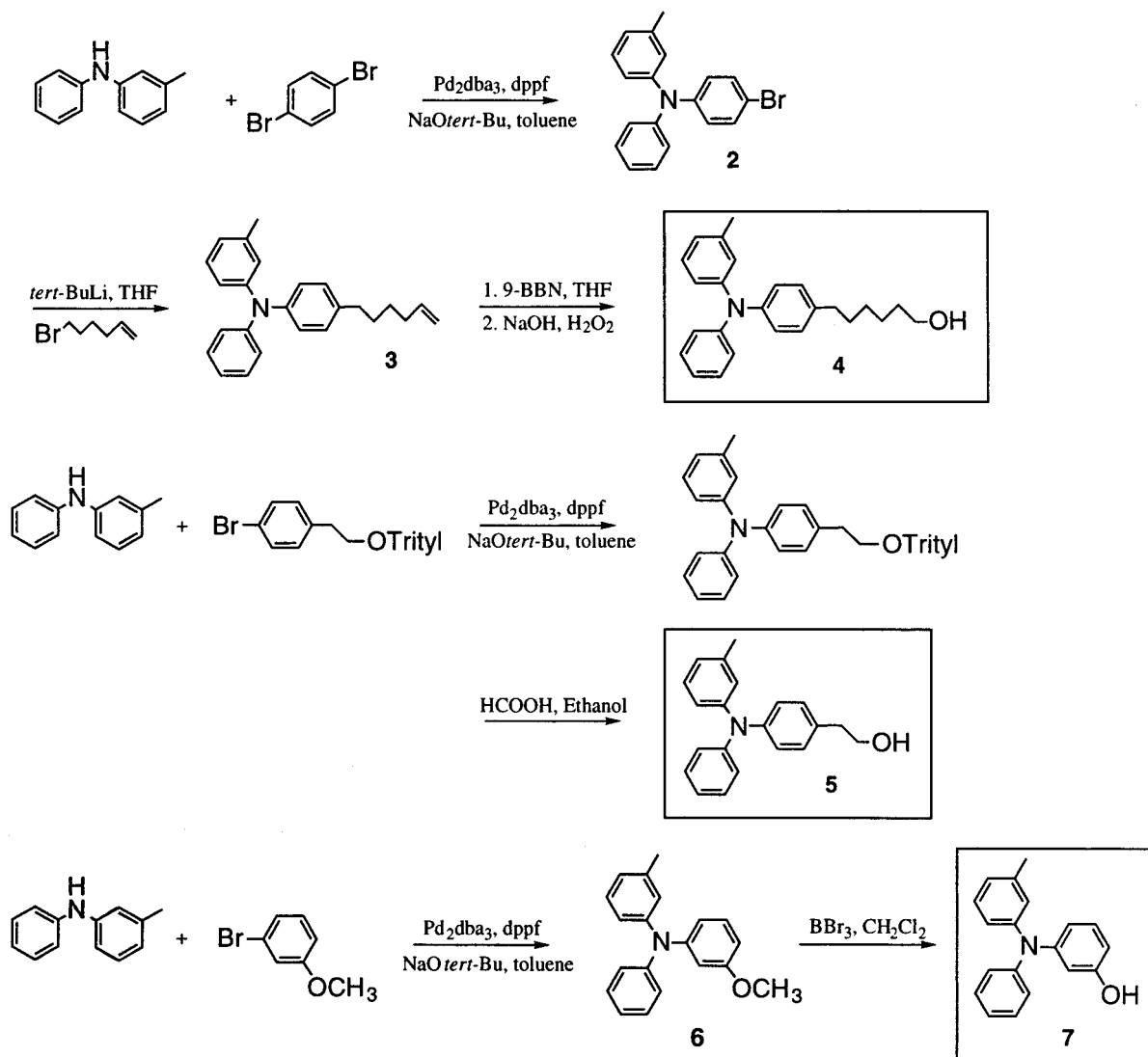
Cross-Linking Procedure. Polymer films were placed 7 in. away from a 150-W Hg:Xe lamp with a glass diffuser between for uniform exposure and irradiated for 1 h.

Results and Discussion

Synthesis. The monomers employed in this study are norbornenes linked to a triarylamine. The linkers contain either an ester or an ether functionality, which varies the polarity around the triarylamine group. Increases in linker length result in a greater number of degrees of freedom for the TPA functionality in the polymer.

The key step of the monomer synthesis is the assembly of a suitably functionalized triarylamine moiety through Pd-catalyzed coupling of a substituted bromobenzene with *m*-tolylphenylamine (Scheme 1). Using

Scheme 1. Synthesis of Functionalized Triarylamines Bearing Alkyl Linkers of Different Lengths



the chemistry developed by Buchwald and Hartwig,^{36–39} the different triarylamines have been obtained in yields of 64–83%.

Alkylation of 1-bromo-4-(*m*-tolylphenylamino)benzene (**2**) with 6-bromohexene followed by reaction with 9-BBN afforded a triarylamine bearing a C_6 -alkyl linker (**4**) (Scheme 1). Attempts to synthesize C_4 , C_3 , and C_2 analogues of **4** from 1-bromo-4-(*m*-tolylphenylamino)benzene failed. 4-Bromobutene and TBS-protected 4-bromobutanol have been tested as C_4 -alkylating agents under conditions similar to those for the synthesis of **3**. In both cases, only *m*-tolylidiphenylamine was isolated. Reaction of allylbromide with **2** under lithiation conditions and reaction of allyl-MgBr with **2** in the presence of a Ni catalyst^{40,41} did not result in formation of the C_3 analogue of **3**. Similarly, reaction of vinyl-MgBr with

2 did not yield the desired product. As illustrated in Scheme 1, a triarylamine bearing a C_2 linker (**5**) was prepared from 4-bromophenethanol, and compound **7** was obtained via Pd-coupling of *m*-bromoanisidine to *m*-tolylphenylamine.

As shown in Schemes 2 and 3, compound **7** can be directly attached to a norbornene acid chloride or norbornene alcohol to produce monomers with a C_0 linker. A *para*-alkoxy substituent would significantly alter the oxidation potential of triarylamine.⁴² Therefore, *meta*-substituted phenol **7** was prepared to ensure that the resulting C_0 polymers are comparable to the polymers bearing C_2 or C_6 linkers.

The ester monomers **8**, **9**, and **10** have been synthesized from the alcohols **4**, **5**, and **7** as shown in Scheme 2.

To prepare the less polar ether monomers, the alcohols **4** and **5** have been transformed to the corresponding iodides⁴³ **11** and **12** and reacted with norborn-2-ene-5-methanol as shown in Scheme 3. In both cases, elimination interfered with ether formation. In the case of

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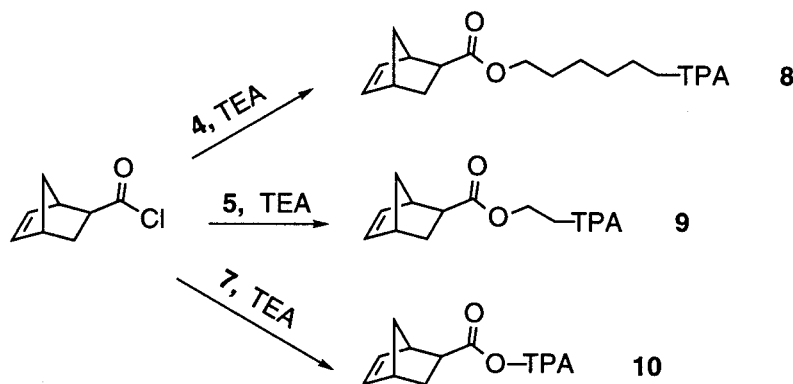
(40) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374.

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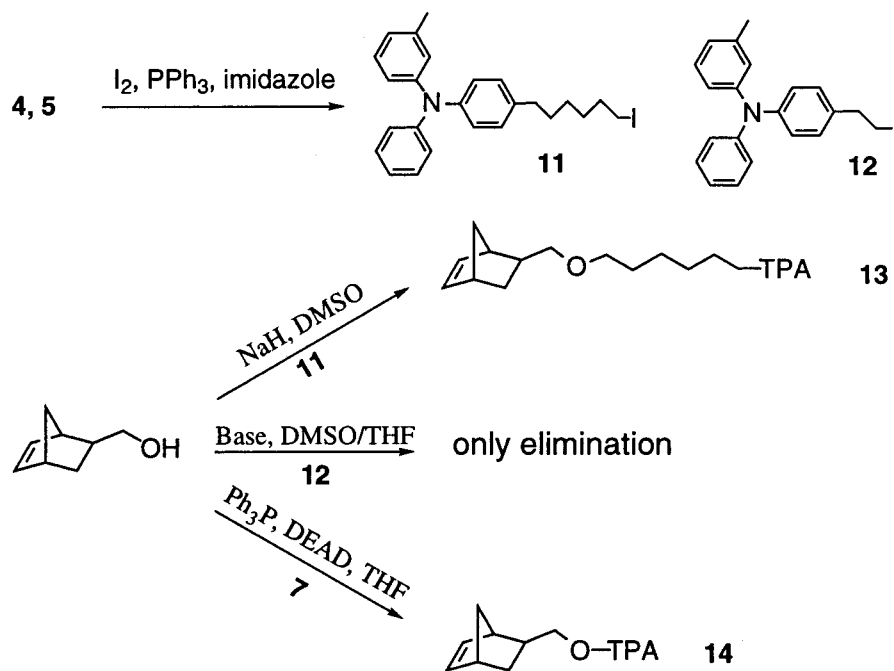
(42) Barlow, S.; Thayumanavan, S.; Marder, S. R. unpublished results.

(43) Millar, J. G.; Underhill, E. W. *J. Org. Chem.* **1986**, *51*, 4727.

Scheme 2. Synthesis of the Monomers Containing Ester Groups



Scheme 3. Synthesis of the Monomers Containing Ether Groups



11, the desired product **13** was isolated in 22% yield along with the elimination product **3**. In the case of **12**, only 1-vinyl-4-(*m*-tolylphenylamino)benzene⁴⁴ was obtained in 60% yield. It has been found that NaH does not react with **11** and **12**, but the elimination is caused by the deprotonated norborn-2-ene-5-methanol. Changing the base therefore had no effect on the ratio of ether formation to elimination. Employing different solvents and lowering the reaction temperature did not improve the yield of the ether. Reaction of alcohols **4** and **5** with norborn-2-ene-5-methyl iodide has been tried but resulted only in decomposition. The C_0 monomer **14** was obtained through coupling of the phenol **7** to norborn-2-ene-5-methanol using Mitsunobu conditions⁴⁵ (Scheme 3).

Initiator **1** was used to polymerize the monomers **8**, **9**, **10**, **13**, and **14**. The polymerization reaction was allowed to proceed for 2.5 h at room temperature in dichloromethane. Treatment with ethyl vinyl ether

(44) An efficient synthesis of 1-vinyl-4-(*m*-tolylphenylamino)benzene, its anionic polymerization, and applications of the polymer as a hole transport material will be reported elsewhere.

(45) Nakano, J.; Mimura, M.; Hayashida, M.; Kimura, K.; Nakanishi, T. *Heterocycles* **1983**, *20*, 1975.

Table 1. Polymerization Results

| polymer | M_n^a | PDI ^a |
|----------------|---------|------------------|
| poly-8 | 48 000 | 1.22 |
| poly-9 | 38 000 | 1.16 |
| poly-10 | 46 000 | 1.13 |
| poly-13 | 62 000 | 1.22 |
| poly-14 | 58 000 | 1.17 |

^a Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

Table 2. Glass Transition Temperatures for the Triarylamine-Substituted Poly(norbornenes)

| $-COO-$ polymer | T_g ($^{\circ}C$) | $-CH_2-O-$ polymer | T_g ($^{\circ}C$) |
|-----------------|-----------------------|--------------------|-----------------------|
| poly-8 | 37.6 | poly-13 | 23.4 |
| poly-9 | 72.6 | | |
| poly-10 | 84.0 | poly-14 | 68.3 |

cleaved the initiator from the polymer chain. The polymers were then isolated and purified by repeated precipitation from dichloromethane with methanol. All polymers were prepared using a monomer-to-initiator ratio of 100. Polydispersities ranged between 1.14 and 1.22 (Table 1). The general structure of the polymers is shown in Figure 4.

As previously observed with liquid crystalline ROMP polymers,²⁴ the T_g decreases with increasing linker

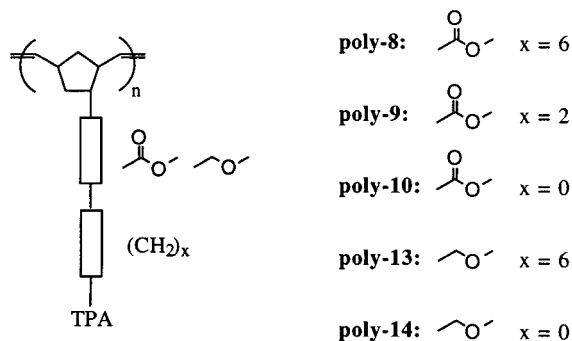


Figure 4. General structure of the hole-transporting poly(norbornenes).

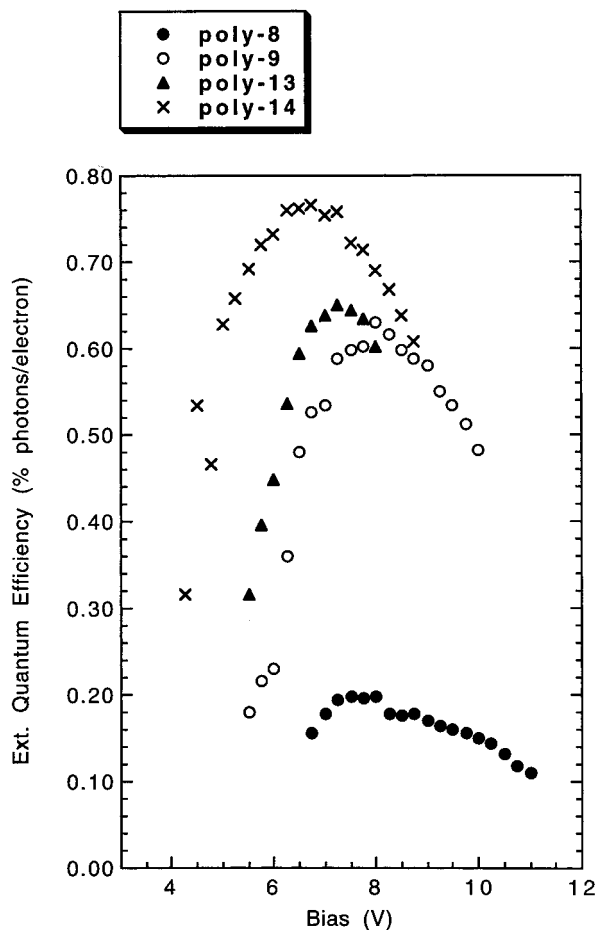


Figure 5. ITO/poly(norbornene)-TPA/Alq₃/Mg: External quantum efficiency vs bias voltage for different triarylamine-substituted poly(norbornenes) as the hole transport layer.

length suggesting that the triarylamine side group has higher mobility (Table 2). Furthermore, the T_g of the ester polymers was found to be significantly higher compared to their ether analogues.

All polymers cross-link upon exposure to UV light. For thin films, irradiation with a 150-W Hg:Xe lamp for 1 h causes the films to become completely insoluble in organic solvents. Addition of a sensitizer is not necessary and does not shorten the time needed for cross-linking. We presume that the triarylamine substituents, which have their absorption maximum at 303 nm, sensitize a photochemical reaction of the carbon-carbon double bonds in the backbone. The UV-irradiated films remain colorless and transparent and retain

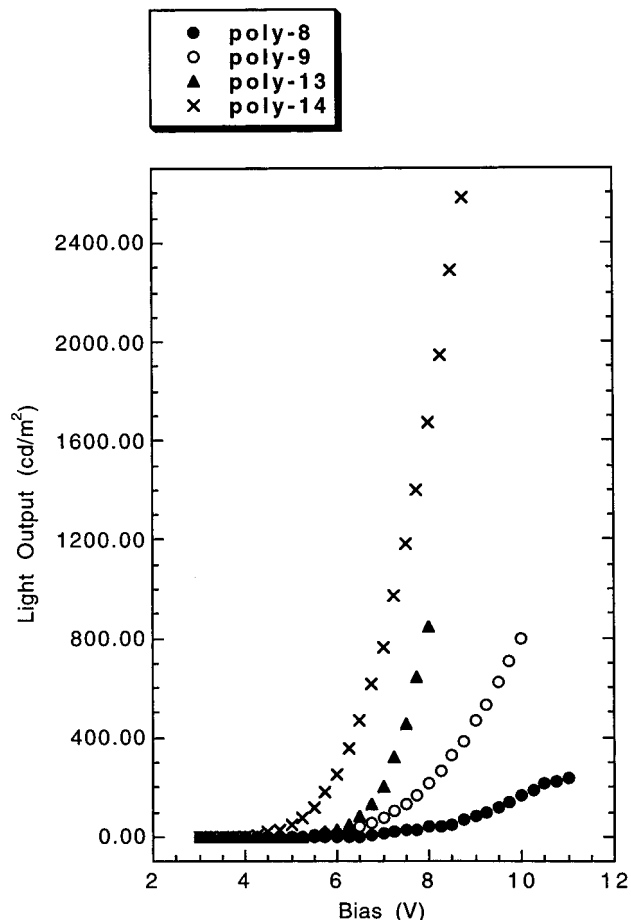


Figure 6. ITO/poly(norbornene)-TPA/Alq₃/Mg: Light output vs bias voltage for different triarylamine-substituted poly(norbornenes) as the hole transport layer.

their blue fluorescence. Details of the cross-linking mechanism are still under investigation.

Fabrication and Characterization of Light-Emitting Devices. Two-layer LEDs have been prepared with **poly-8**, **poly-9**, **poly-10**, **poly-13**, and **poly-14** as the hole transport layer (HTL). Indium tin oxide (ITO) was used as the anode, Mg as the cathode (200 nm), and tris(8-quinolinato)aluminum (Alq₃) as the electron-transporting and emitting layer (50 nm). The light emission corresponded to the typical Alq₃ emission spectrum^{7,8} resulting in green LEDs.

All of the studied polymers have very good solubilities in organic solvents, and spin casting from chlorobenzene yielded uniform thin films of good quality. A thinner HTL results in a decreased device operating voltage. However, when the HTL gets too thin, the external quantum efficiency starts to decrease (Table 3). The device data reported in Table 4 and Figures 5–8 refer to 20 nm thick HTL films, which showed the highest external power efficiency.

Table 4 and Figures 5–8 summarize the device data for the hole-transporting poly(norbornenes). All of the studied polymers exhibit high quantum efficiencies. The small structural differences among the five polymers have a large impact on the device performance, showing that reducing the polarity and length of the linker greatly improves the characteristics (compare **poly-8** (C₆/ester) to **poly-14** (C₀/ether)).

Poly-10 (C₀/ester) decomposed rapidly under device operating conditions. Separation of the carbonyl group

Table 3. ITO/poly-14/Alq₃/Mg: Dependence of the Device Performance on the Thickness of the Hole Transport Layer

| HTL film thickness (nm) ^a | operating voltage (V) ^b | max external quantum efficiency (% photons/e ⁻) | max light output (cd/m ²) | max external power efficiency (lm/W) |
|--------------------------------------|------------------------------------|-------------------------------------------------------------|---------------------------------------|--------------------------------------|
| 30 | 5.25 | 0.81 | 1690 @ 11 V | 1.21 |
| 20 | 4.25 | 0.77 | 2580 @ 8 V | 1.30 |
| 15 | 3.25 | 0.62 | 3150 @ 7 V | 1.23 |

^a Determined by TINCOR alpha-step profilometer. ^b Light output at this voltage equals 5 cd/m².

Table 4. ITO/poly(norbornene)-TPA/Alq₃/Mg: Device Performance for Different Hole Transporting Polymers^a

| HTL polymer | operating voltage (V) ^a | max external quantum efficiency (% photons/e ⁻) | max light output (cd/m ²) | max external power efficiency (lm/W) |
|-------------------------------------|------------------------------------|-------------------------------------------------------------|---------------------------------------|--------------------------------------|
| -COO- poly-8 | 6.75 | 0.20 | 240 @ 11 V | 0.26 |
| -COO- poly-9 | 5.50 | 0.63 | 800 @ 10 V | 0.84 |
| -COO- poly-10 | (8) ^c | (0.42) ^c | (1030 @ 14 V) ^c | (0.54) ^c |
| -CH ₂ -O- poly-13 | 5.50 | 0.65 | 850 @ 8 V | 0.96 |
| -CH ₂ -O- poly-14 | 4.25 | 0.77 | 2580 @ 8 V | 1.30 |
| cross-linked poly-14 | 5.25 | 0.37 | 880 @ 9 V | 0.61 |

^a All data refer to 20 nm thick HTL films. Cross-linking of **poly-14** was achieved by UV irradiation after spin casting on ITO. ^b Light output at this voltage equals 5 cd/m². ^c Degradation interfered with measurement.

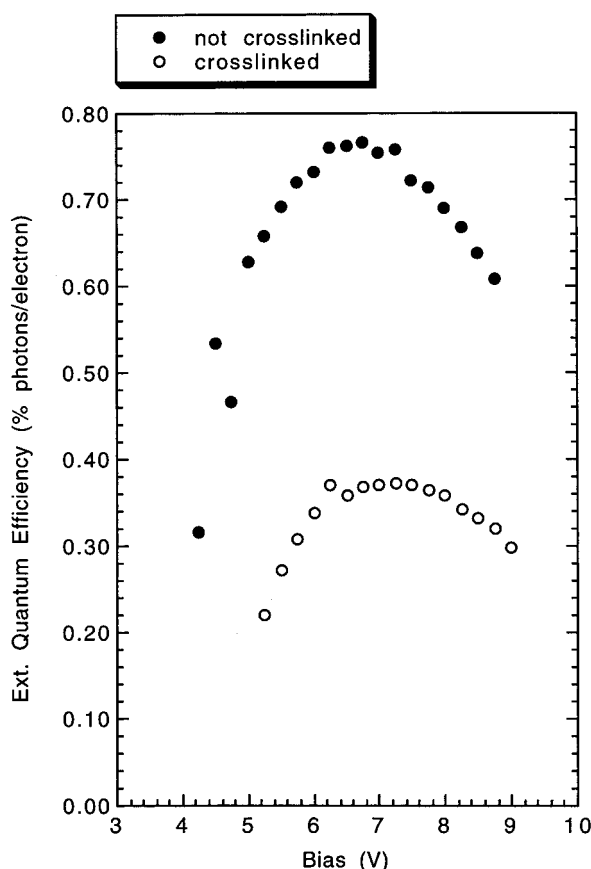


Figure 7. ITO/poly-14/Alq₃/Mg: Effect of cross-linking of the hole transport layer on the external quantum efficiency of the device.

from the triarylamine functionality by an alkyl segment results in increased stability of the device (**poly-9**, **poly-8**). The ether polymers **poly-13** and **poly-14** show the best stabilities, presumably since they lack the carbonyl group as a reaction center, which reduces the number of possible decomposition pathways.

Substitution of the ester functionality by the less polar ether linkage causes the external quantum efficiency to increase and the operating voltage to decrease significantly (Table 4; Figures 5 and 6). In the case of **poly-13** and **poly-8**, a 3-fold increase in external quantum efficiency has been achieved by substituting carbonyl groups with the nonpolar methylene groups.

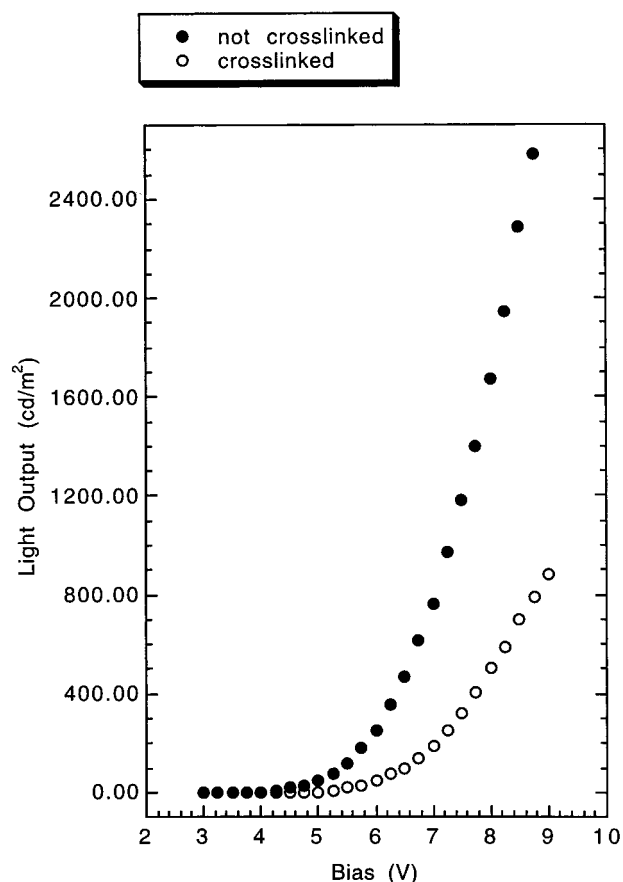


Figure 8. ITO/poly-14/Alq₃/Mg: Effect of cross-linking of the hole transport layer on light output.

On the basis of the disorder formalism developed by Bässler and Borsenberger^{2,3,6} the hole mobilities in the less polar polymers, that is, the polymers with linkers containing an ether functionality, should be higher. The disorder model assumes that the charge transport occurs through hopping between localized electronic states, which show a Gaussian-shaped distribution. According to the model, energetical disorder, e.g., the presence of several functional groups with different polarities, results in broadening of the distribution of states and, consequently, in lower charge mobilities. Thus, our results on two-layer devices using a hole transport layer and Alq₃ as an emitting layer suggest

that the quantum efficiency can be improved and the operating voltage decreased by increasing the hole mobility of the HTL. One caveat of that analysis is the possible influence of the polymer structure on the position of the highest occupied molecular orbital (HOMO) of the triarylamine moieties. The relative position of the energy levels of the hole transport and light-emitting moieties is expected to affect the performance of two-layer devices as well. Independent mobility measurements by time-of-flight experiments and energy level determination will provide more information. These experiments will be performed in future work.

By introducing longer alkyl linkers, we have increased the number of degrees of freedom available to the triarylamine side groups. It has been previously found for carbazole-containing polymers that increased mobility of the hole-conducting side groups enhances the hole mobility.⁴⁶ An optimum linker length has been shown to exist in this study. In our system, however, we see a decrease in efficiency and an increase in operating voltage with increasing linker length (**poly-8** vs **poly-9** and **poly-13** vs **poly-14**). The polymers with the shortest linkers show the best performance. If side group mobility promotes hole transport in our system, this influence is overcompensated by the fact that longer alkyl linkers correspond to more insulating matter around the hole-transporting functionalities. Thus, with increasing linker length, the density of triarylaminates becomes lower, resulting in less efficient charge transport and decreased device performance.

All of the studied polymers can be cross-linked by a simple procedure, which does not require addition of other reagents or removal of byproducts. Cross-linked devices show poorer performance relative to the ones with the original soluble films (Table 4; Figures 7 and 8). Possible explanations are partial decomposition of the polymers in UV light and decreased film quality as a consequence of slight volume changes upon cross-

linking. Decreased mobility of the triarylamine side groups may also contribute to a reduced charge transport efficiency. A cross-linkable HTL allows us to fabricate and study two-layer devices with a spin cast polymer as an emitting layer. Experiments using a PPV derivative as an EL are in progress.

Conclusions

We have synthesized a series of cross-linkable polymeric hole transport materials and demonstrated their influence on the performance of organic two-layer LEDs (ITO/poly(norbornene)-TPA/Alq₃/Mg). Poly(norbornenes) with pendant triarylamine groups have proven to yield devices with high external quantum efficiencies and light output. The device performance improved as a result of slight changes in the polymer backbone. The least polar polymer with the shortest linker showed the highest external quantum efficiency (0.77%), the lowest operating voltage (4.25 V), and the best device stability.

The film formation properties of these poly(norbornenes) are excellent, allowing efficient fabrication of thin (20 nm and thinner) HTL films through spin casting. The HTL films can be easily cross-linked by UV irradiation. Cross-linking, however, has been found to decrease device performance. The maximum external quantum efficiency for the best material dropped from 0.77% to 0.37%.

For our future work, we conclude that avoiding polar functional groups and long spacers in the polymer backbone will yield promising hole transport materials for LED and laser applications. We are currently developing synthetic procedures for triarylamine-containing polymers with all-hydrocarbon backbones.

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