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Novel Blue Light Emitting Polymer Containing an Adamantane Moiety

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Burroughes et al. first introduced conjugated poly(phenylenevinylene) (PPV) as an organic electroluminescent (EL) material for light-emitting diodes (LED) in 1990.[1] Tremendous progress has been made since then in the discovery of new polymers and in the performance of the related LED devices.[2] The colors emitted by the current polymers span almost the whole range of the visible spectrum with the exception of blue. Stable, efficient, and high-brightness blue light emitting materials are desirable for full color display applications. These materials can also serve as energy-transfer donors in the presence of lower energy fluorophores.[3] Recent material research has been focused on the synthesis of polymers with large energy band gaps to emit blue light.[4−8]

An effective approach to achieve large energy band gaps for blue light is to control the conjugation length. For example, the introduction of meta linkages in the PPV type of polymers leads to the interruption of conjugation.[9] An alternative approach is to incorporate the well-defined conjugated chromophores in polymer side chains[10] or main chains. In the latter case, the conjugation length of the chromophores can be controlled by introducing flexible nonconjugated spacer groups. This approach has been demonstrated in several examples.[11] However, the incorporation of such flexible spacers into a rigid conjugated polymer backbone reduces its stiffness, thus affecting the microscopic molecular order of the polymer[12] and also leading to high turn-on and operating voltages.

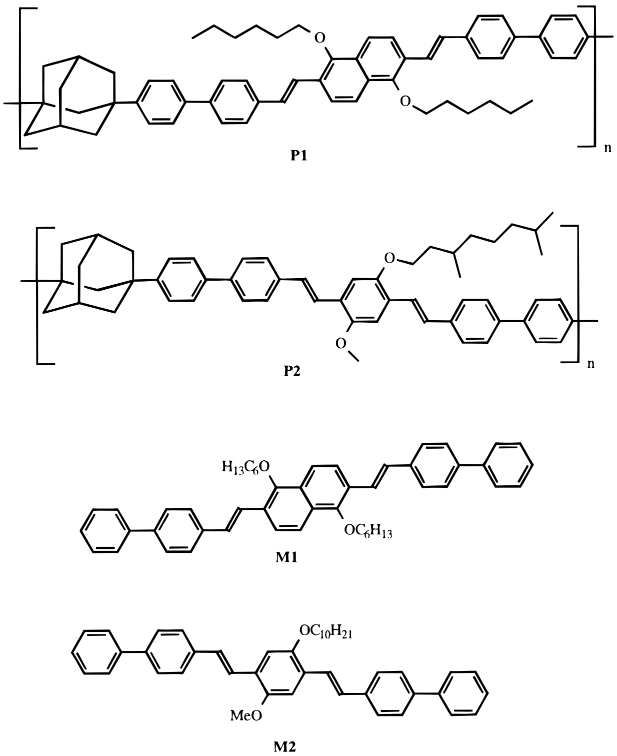

Figure 1. Chemical structures of polymers and model compounds.

In this paper, we report on the design, synthesis, and characterization of a new blue light emitting polymer **P1** (Figure 1) containing adamantane as a rigid spacer group. For comparison, a similar green light emitting polymer **P2** containing a phenylenevinylene (PV) segment has been synthesized. Adamantane has been incorporated into polymers because of its rigid and spherical structure, which provides unusual physical and thermal properties.[13] The incorporation of the adamantane spacer group is expected to increase the glass transition temperature (T_g), thermal stability, chain rigidity, and solubility, to reduce crystallinity, and to prevent the aggregation of chromophores in the solid state.[14] Compared with **P2**, the use of electron-rich and more bulky naphthalene units modifies the band structure and molecular conformation of the polymer.[15] The degree of conjugation between the naphthalene moiety and the vinyl double bond, naphthalenevinylene (NV), is lower compared with that between a benzene ring and

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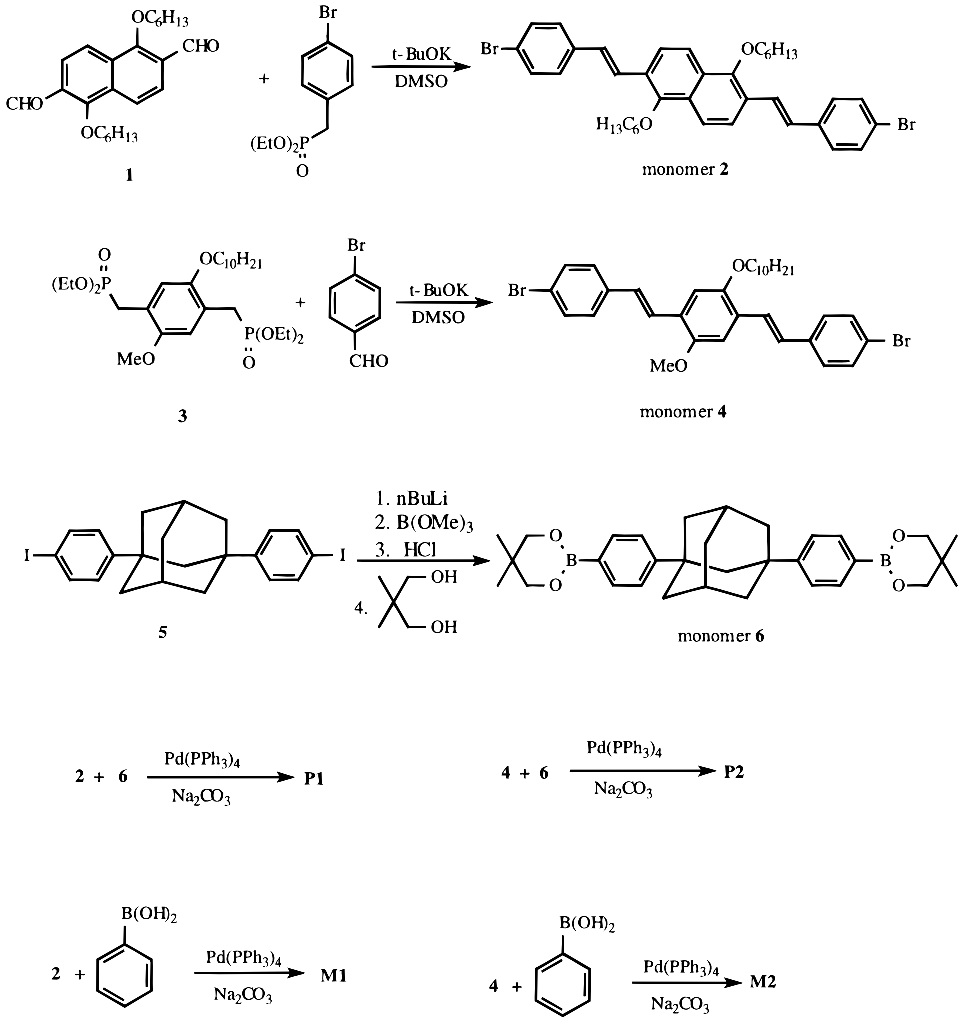
Scheme 1. Synthesis of Polymers and Model Compounds



a vinyl double bond (PV), resulting in a shorter effective conjugation length and a blue shift in emission.[16] Thus, we can effectively control the conjugation length of the polymer to tune the emitting color. The long side chains in both polymers are introduced to enhance the solubility of the polymers. To demonstrate the concept that adamantane is an effective spacer, two model compounds, **M1** containing a NV segment and **M2** containing a PV segment, were synthesized.[17]

The synthesis is shown in Scheme 1. Compounds **1** and **3** were synthesized according to modified literature procedures.[18,19] Monomers **2** and **4** were prepared by the Horner–Emmons reaction and are highly fluorescent crystals.[20] The large alkene coupling constants of 17 Hz observed in the ^{1}H NMR spectra and the FTIR band at 960 cm^{-1} indicate exclusive *trans*-olefin bonds. Monomer **6** was synthesized from its diiodide precursor **5**.[21,22] The synthesis of the model compounds and the polymerization were carried out via the Suzuki coupling reaction.[23] The model compounds and polymers are highly fluorescent materials. **M1** and **P1** are blue fluorescent, while

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(17) **M1**: recrystallized from toluene to give a greenish crystal at 65% yield; ^{1}H NMR (CDCl$_3$) δ 0.97 (t, J = 6.7 Hz, 6H, CH$_3$), 1.41–1.68 (m, 12H, alkyl), 2.00–2.03 (m, 4H, alkyl), 4.06 (t, J = 6.4 Hz, 4H, OCH$_2$), 7.25–7.95 (m, 26H, aromatic and vinyl H); ^{13}C NMR (CDCl$_3$) δ 14.09, 22.75, 26.14, 30.55, 31.84, 75.78, 118.76, 123.33, 123.70, 126.45, 126.95, 127.03, 127.36, 127.44, 128.84, 129.02, 129.66, 136.89, 140.44, 140.74, 153.36; mp 170–172 °C; FD-MS *m*/*z* 684 (M$^+$). **M2**: recrystallized from toluene to give a greenish-yellow crystal at 67% yield; ^{1}H NMR (CDCl$_3$) δ 0.86 (d, J = 6.6 Hz, 6H, terminal CH$_3$), 1.01 (d, J = 6.4 Hz, 3H, CH$_3$), 1.17–1.98 (m, 11H), 3.94 (s, 3H, OCH$_3$), 4.09–4.14 (m, 2H, OCH$_2$), 7.12–7.63 (m, 24H, aromatic and vinyl H); ^{13}C NMR (CDCl$_3$) δ 19.83, 22.63, 22.72, 24.88, 28.03, 30.17, 36.62, 37.50, 39.31, 56.44, 67.94, 109.32, 110.64, 123.42, 123.64, 126.92, 126.97, 127.04, 127.31, 127.34, 127.45, 127.54, 128.41, 128.50, 128.81, 137.02, 137.09, 140.17, 140.79, 151.63; mp 198–200 °C; FD-MS *m*/*z* 620 (M$^+$).

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(19) Compound **1**: recrystallized from hexane to a give light yellow powder at 65% yield; ^{1}H NMR (CDCl$_3$) δ 0.93 (t, J = 6.7 Hz, 6H, CH$_3$), 1.37–1.42 (m, 8H, alkyl), 1.55–0.60 (m, 4H, alkyl), 1.95–2.00 (m, 4H, alkyl), 4.15 (t, J = 6.7 Hz, 4H, OCH$_2$), 7.92 (d, J = 8.8 Hz, 2H, naphthyl), 7.89 (d, J = 8.8 Hz, 2H, naphthyl), 10.60 (s, 2H, CHO); ^{13}C NMR (CDCl$_3$) δ 14.01, 22.59, 25.65, 30.25, 31.63, 79.50, 119.53, 123.69, 127.51, 133.19, 161.56, 189.51; mp 50–52 °C; FD-MS *m*/*z* 384 (M$^+$). Compound **3**: recrystallized from hexane to give a white waxy crystal; ^{1}H NMR (CDCl$_3$) δ 0.86 (d, J = 6.5 Hz, 6H, terminal CH$_3$), 0.93 (d, J = 6.5 Hz, 3H, CH$_3$), 1.13–1.85 (m, 21H, CH$_3$ of PO(CH$_2$CH$_3$)$_2$ and alkyl), 3.12 (dd, J_1 = 20.5 Hz, J_2 = 4.8 Hz, 4H, benzylic), 3.80 (s, 3H, OCH$_3$), 3.94–4.01 (m, 10H, CH$_2$ of PO(CH$_2$CH$_3$)$_2$ and OCH$_2$ of alkyloxy), 6.91 (s, 1H, aromatic), 6.94 (s, 1H, aromatic); ^{13}C NMR (CDCl$_3$) δ 16.33, 16.41, 19.72, 22.61, 22.71, 24.73, 28.00, 29.95, 36.54, 37.39, 39.29, 56.17, 61.86, 61.94, 67.41, 114.05, 114.06, 115.09, 115.11, 119.35, 119.39, 119.46, 119.50, 119.57, 119.61, 119.68, 119.72, 150.55, 150.58, 150.64, 150.67, 150.95, 150.98, 151.03, 151.07; mp 32–34 °C; FD-MS *m*/*z* 532 (M$^+$).

M2 and **P2** are green fluorescent. The polymers are soluble in organic solvents such as THF, chloroform, and 1,2-dichloroethane. A pinhole-free thin film was obtained easily by spin-coating. The molecular weight of the polymers were determined by size-exclusion chromatography (SEC) using polystyrene standards in THF. **P1** has a weight-average molecular weight (M_w) of 17 900 with a polydispersity of 2.30, and **P2** has a M_w of 18 800 and a polydispersity of 1.79.

The polymers possess excellent thermal stability. **P1** shows an onset thermal decomposition temperature (T_d) at 362 °C and a T_g at 151 °C. **P2** has a T_d of 411 °C and a T_g of 152 °C. The results indicate that the adamantane moiety increases the rigidity of the polymer main chain, resulting in high T_g and T_d. A relatively low T_g has been reported for polymers containing flexible spacer groups.[24] No other thermal transitions were observed for both polymers before their T_d. This is consistent with our design that the adamantane moiety decreases possible crystallinity and thus offers an amorphous homogeneous polymer.

The UV−vis and photoluminescence (PL) spectra of the model compounds and polymers in toluene, obtained with a FluoroMax-2 spectrometer, are shown in Figure 2. The UV−vis spectra of **M1** and **P1** are almost identical. Both have strong absorption bands at 373 and 395 nm, which might be attributed to the $\pi-\pi^*$ transition of the conjugated segment. Similarly, **M2** and **P2** show almost identical absorption spectra, with λ_{max} at 407 nm. The blue shift of λ_{max} of **P1** relative that of **P2** suggests that incorporation of the naphthalene unit into the backbone twists the vinyl double bond out of the plane of the aromatic ring more than a simple benzene and forces the π conjugation to be less extended. This explanation is also supported by the PL spectra.

In a dilute solution, **P1** and **M1** show almost identical PL spectra. This is also observed for **P2** and **M2**. The almost identical UV−vis and PL spectra of the model compounds and the polymers confirm our design that the active chromophores in solution are the NV and PV segments for **P1** and **P2** and that the adamantane unit is an efficient π-conjugation interrupter. In solid thin films, the main emission peaks of the polymers shift to longer wavelength (Figure 3). **P1** showed blue emission at 470 nm while **P2** had green emission at 516 nm.

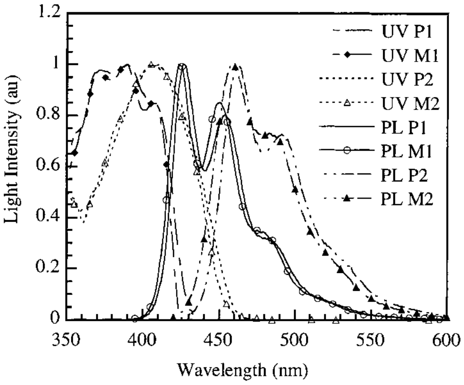

Figure 2. UV−vis and PL spectra of polymers and model compounds in solution.

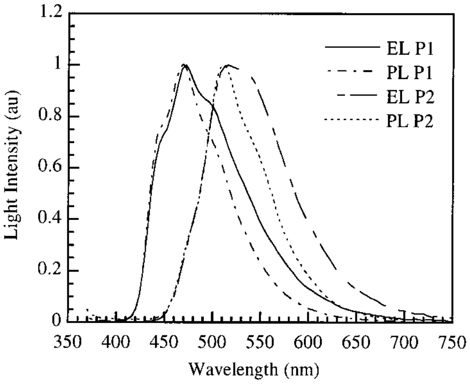

Figure 3. EL and PL (solid thin film) of the polymers.

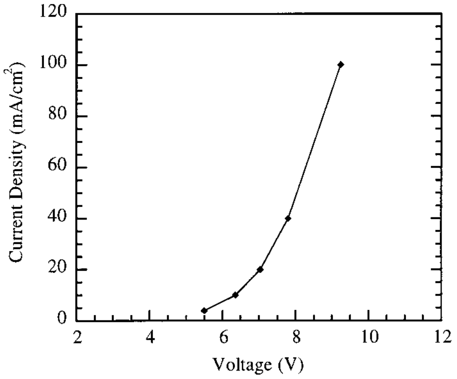

Figure 4. Current density−voltage characteristic for a single-layer LED device fabricated from **P1**.

Single-layer LED devices indium−tin oxide (ITO)/polymer/Mg:Ag were fabricated by spin-coating the polymer solution onto an ITO-coated glass substrate. The coating thickness was about 700 Å, and the active device area was 0.1 cm^2. All of the devices exhibited typical diode behavior. The EL spectra of the polymers are shown in Figure 3. **P1** showed blue emission at 470 nm where the PL emission also appeared. **P2** emitted green light at 516 nm, which overlapped with the PL emission peak. These results suggest PL and EL might experience similar excited states. The turn-on voltage of the **P1** LED is 5.5 V (Figure 4). Thus, we have

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(20) Monomer **2**: recrystallized three times from toluene to give light yellow fine needle crystals at 50% yield; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 6.7 Hz, 6H, CH_3), 1.41−1.43 (m, 8H, alkyl), 1.63−1.68 (m, 4H, alkyl), 1.92−1.97 (m, 4H, alkyl), 4.00 (t, J = 6.4 Hz, 4H, OCH_2), 7.13 (d, J = 16.5 Hz, 2H, vinyl), 7.42 (d, J = 8.4 Hz, 4H, phenyl), 7.50 (d, J = 8.4 Hz, 4H, phenyl), 7.60 (d, J = 16.5 Hz, 2H, vinyl), 7.74 (d, J = 8.8 Hz, 2H, naphthyl), 7.88 (d, J = 8.8 Hz, 2H, naphthyl); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.72, 26.12, 30.50, 31.80, 75.83, 118.81, 121.40, 123.62, 123.94, 126.21, 128.01, 128.26, 129.71, 131.87, 136.75, 153.47, 176.88; mp 170−172 °C; FD-MS *m*/*z* 688 (M^+). Monomer **4**: recrystallized from toluene three times to give an orange-red solid at 50% yield; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 6.5 Hz, 6H, terminal CH_3), 0.98 (d, J = 6.5 Hz, 3H, CH_3), 1.37 (m, 8H, alkyl), 1.15−1.95 (m, 10H, alkyl), 3.91 (s, 3H, OCH_3), 4.07 (t, J = 6.5 Hz, 2H, OCH_2), 7.05 (d, J = 17.6 Hz, 2H, vinyl), 7.36−7.48 (m, 12H, vinyl 2H and aromatic); ^{13}C NMR ($CDCl_3$) δ 19.80, 22.61, 22.70, 24.85, 28.01, 30.15, 36.54, 37.44, 39.28, 56.30, 67.85, 109.26, 110.59, 121.15, 121.17, 124.04, 124.27, 126.52, 126.76, 127.75, 127.81, 127.97, 128.05, 131.75, 131.77, 136.84, 136.92, 151.22, 151.56; mp 106−108 °C; FD-MS *m*/*z* 624 (M^+).

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(22) Monomer **6**: recrystallized from toluene to give pure product as a white solid (25% yield in two steps); ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 12H, CH_3), 1.78 (s, 2H), 1.96 (s, 8H), 2.05 (s, 2H), 2.30 (s, 2H), 3.74 (s, 4H, CH_2), 7.37 (d, J = 8.1 Hz, 4H, aromatic), 7.75 (d, J = 8.1 Hz, 4H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.91, 29.60, 31.87, 35.97, 37.46, 42.23, 48.59, 72.28, 124.17, 128.16, 133.87, 153.21; mp 249−251 °C; FD-MS *m*/*z* 512 (M^+).

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demonstrated that our adamantane-containing polymers show relatively low turn-on voltages compared with polymers containing other saturated and nonconjugated spacer groups.[25]

In summary, we have synthesized and characterized new light-emitting polymers containing a rigid adamantane moiety in the polymer main chain. These polymers show good solubility and excellent thermal stability. The incorporation of the adamantane units significantly increases the T_g and T_d of the polymers. Moreover, the adamantane unit is an efficient π-conjugation interrupter. In addition, blue light emission and low turn-on voltage were obtained from a single-layer LED fabricated from **P1**. LED made from **P2** emitted bright green light. By rational design of the chromophores, we were able to effectively control the conjugation length to tune the emitting color of the LED devices.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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