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# NEW LUMINESCENT POLYMERS FOR LEDS AND LECS

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Abstract: Statistical copolymers **5** containing poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV) and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) have been synthesized using the dehydrohalogenation condensation route. The copolymers show a shift of photoluminescence maxima to longer wavelengths as the proportion of the MEH-PV unit increases. This trend is accompanied by reduced efficiencies and lower turn-on voltages in single layer electroluminescent devices. Light-emitting electrochemical cells (LECs) have been prepared using a blend of DMOS-PPV **1** with poly(ethylene oxide)/lithium triflate and the homopolymer poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylene vinylene] (MTEM-PPV) **9** with lithium triflate. In comparison with single-layer devices which were fabricated using the homopolymers **1** and poly[2,5-bis(triethoxymethoxy)-1,4-phenylene vinylene] (BTEM-PPV) **10**, the LEC devices showed lower turn-on voltages.

## INTRODUCTION

Electroluminescence from light-emitting diodes (LEDs) using PPV as the emissive layer (Ref. 1) has stimulated the synthesis of many new polymers based on derivatives of PPV. Methods used to obtain these polymers include the soluble polymer precursor routes (Refs. 2-5), the dehydrohalogenation polymerization route (Refs. 6-10) to produce soluble polymers directly and the more recent chemical vapor deposition method to produce pinhole free films (Refs. 11, 12). Copolymerizations have also been exploited to enhance the

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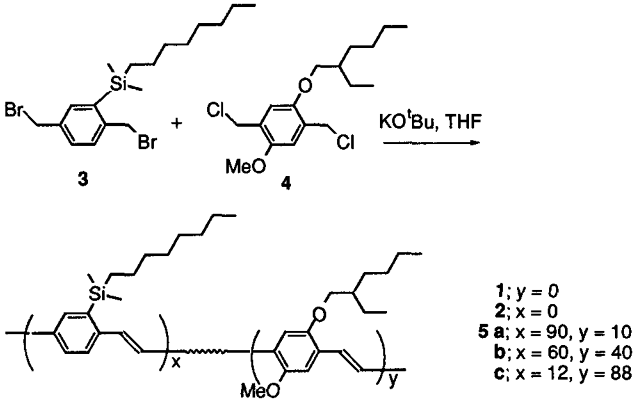
chemical and electrical properties of the luminescent polymers (Ref. 13). This method, additionally, provides the avenue to incorporate two or more desirable functionalities into a single polymer which would otherwise be inherent only in the homopolymers.

We recently described the synthesis and electroluminescent properties of poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV) **1** (Ref. 14). Although DMOS-PPV **1** produced high efficiencies in its single-layer LED (ITO/**1**/Al) devices, the high turn-on voltage of 15 V for observable light emission could be a disadvantage. Hence, in the search for novel copolymers, we have combined the features of **1** with that of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) **2** (Scheme 1) to give poly(DMOSPV-co-MEHPV) **5**. We report here the trends observed in the optoelectronic properties of the copolymers **5** with the changing ratio of each component.



Scheme 1 Synthetic route to poly(DMOSPV-co-MEHPV) **5**

## RESULTS AND DISCUSSION

### The synthesis and characterization of the homopolymers 5.

The synthesis of copolymers **5** is shown in Scheme 1 above. We explored the copolymerization of the silylated bis(bromomethyl) monomer **3** with the corresponding bis(chloromethyl) monomer for MEH-PPV, **4**. The poly(DMOSPV-co-MEHPV) statistical copolymers were obtained in good yield and were totally soluble in common organic solvents such as chloroform, tetrahydrofuran and toluene. The copolymer compositions were found to agree closely with the monomer feed ratios (Table 1), suggesting that both the monomers have almost equal reactivities towards polymerization.

Table 1. Compositions, molecular weights, polydispersities and yields of the copolymers 5

| Copolymers 5 | 5a | 5b | 5c |
|---|---|---|---|
| Monomer feed ratio (3:4) | 10 : 1 | 1 : 1 | 1 : 10 |
| Polymer composition (x:y)[a] | 90 : 10 | 60 : 40 | 12 : 88 |
| Molecular weight ($\overline{M}_w$)[b] | 82 000 | 93 000 | 58 000 |
| Polydispersity[b] | 4.3 | 4.8 | 5.3 |
| Polymer Yield (%) | 80 | 65 | 72 |

[a] Composition determined from silyl-methyl and methoxy protons in $^1$H-NMR;
[b] GPC in $CHCl_3$ using polystyrene as standards.

The UV-VIS spectra of films of DMOS-PPV, copolymers **5a**-**5c** and MEH-PPV are shown in Figure 1. The absorption maxima of the DMOS-PPV and MEH-PPV are at about 414 nm and 500 nm, respectively. The absorption maxima and band edges of the copolymers shift to longer wavelengths with increasing MEHPV content.

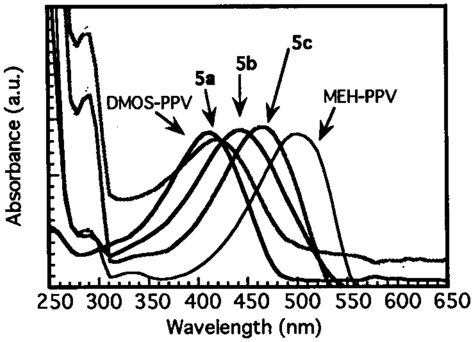


Figure 1. UV-VIS spectra of polymer films of DMOS-PPV **1**, **5a-c** and MEH-PPV **2**

The photoluminescence (PL) emission maxima of the copolymers **5a**, **5b** and **5c** showed a shift to longer wavelengths (Figure 2) as the proportion of MEHPV units in the copolymers was increased, giving green, yellow and orange-red emission, respectively (Ref. 15). The PL quantum efficiencies for solid films of **5a-c** were found to be between those of DMOS-PPV (60%) (Ref. 16) and MEH-PPV (15 %) (Ref. 17). The efficiencies decreased as the ratio of MEHPV content increased, and this trend was also seen in the electroluminescence (EL) efficiencies of ITO/**5**/Al single layer devices (Table 2).

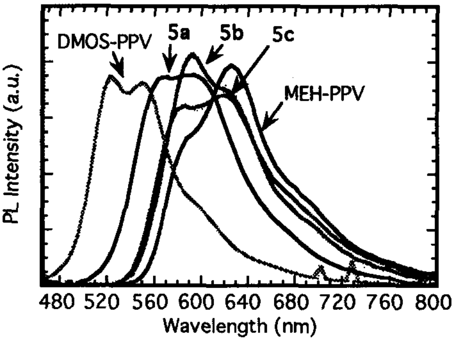


Figure 2. PL spectra of polymer films of DMOS-PPV **1**, copolymers **5a-c** and MEH-PPV

The turn-on voltages reduce in the order of copolymer **5a** < **5b** < **5c** (Table 2).

Table 2. Absorption maxima, PL and EL efficiencies, and turn-on voltages of the devices constructed with polymers **1**, **2** and **5a-5c**

| Polymers | DMOS-PPV **1** | **5a** | **5b** | **5c** | MEH-PPV **2** |
|---|---|---|---|---|---|
| UV $\lambda_{max}$[a](nm) | 414 | 420 | 444 | 464 | 500 |
| PL emission maximum[a] (nm) | 523 | 567 | 600 | 618 | 626 |
| PL efficiency (%) | 60 | 41 | 21 | 18 | 15 |
| EL efficiency (%) | 0.2 | 0.1 | 0.03 | 0.02 | 0.02 |
| Turn-on voltages (V) | 15 | 12 | 7 | 6 | 4 |
| Reduction onset potential[b] (V) | -1.60 | -1.75 | -2.00 | -1.9 | -1.8 |
| Oxidation onset potential[b] (V) | 1.10 | 0.85 | 0.80 | 0.75 | 0.47 |

[a] Measurements on polymer thin films; [b] Cyclic voltammetry measurements were performed on thin films of the polymers on a platinum working electrode with Ag wire as the reference electrode calibrated against Fc/Fc$^+$ 0.42 V, scan rate 20 mV/s. The electrolyte used was 0.1 M tetrabutylammonium perchlorate ($Bu_4NClO_4$) in MeCN (dried over $CaH_2$).

This trend follows the general behavior of the oxidation onset potential in the series **1**, **5a**, **5b**, **5c** and **2** but there is no corresponding trend for the onset of reduction potentials. It is therefore tempting to ascribe this reduction in turn-on voltages to the decreasing barrier to hole injection.

Light-emitting electrochemical cells (LECs).

The new generation of light-emitting electrochemical cells (LECs) developed by Pei *et. al* (Refs. 18-21) has generated world-wide interest. We used the highly luminescent DMOS-PPV **1** in a blend with lithium triflate-doped poly(ethylene oxide) (PEO) to investigate its potential as the emissive layer in fabricating such a device. We found that the single layer devices had a lower turn-on voltage of 4 V in both forward and reverse biases, giving the expected green light emission (maximum of 520 nm). Typical current-voltage characteristics are indicated in Figure 3.

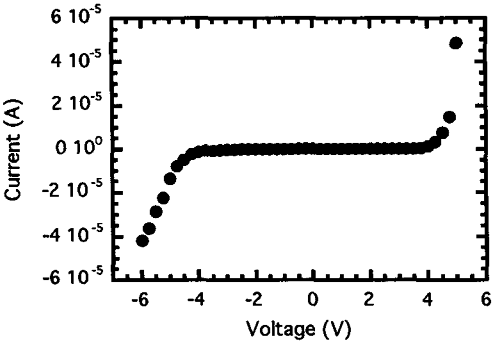
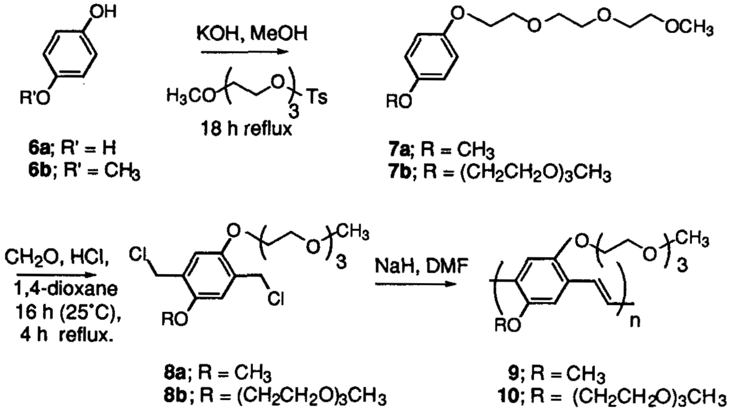


Figure 3. I-V characteristics of a LEC device fabricated with configuration indium tin oxide ITO / **1** + PEO + LiOTf / Al

Although the role of the phase-separated polyelectrolyte may be essential to the function of ionic transport, we considered the synthesis of emissive polymers which contain ion-transporting side chains (Ref. 22). We synthesized homopolymers poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylene vinylene] or MTEM-PPV **9** and the poly[2,5-bis(triethoxymethoxy)-1,4-phenylene vinylene] (BTEM-PPV) **10** with polyether side chains attached to the aromatic ring of a PPV analog (Scheme 2).

Polymerization of monomers **8a** and **8b** by base-promoted dehydrohalogenation using KO$^t$Bu in THF produced insoluble polymers which precipitated from the reaction medium. We then attempted the NaH/DMF base/solvent system as proposed by Garay et al. (Ref. 23), and the resultant polymer remained in solution during the reaction even with excess base to give polymers with reasonable molecular weights (Table 3).



Scheme 2. Synthetic route to polymers MTEM-PPV **9** and BTEM-PPV **10**

Both **9** and **10** absorb at a maximum wavelength of 494 and 498 nm in the UV-VIS, respectively (Figure 4), and emit in the red (601 and 640 nm, respectively). They therefore resemble MEH-PPV, although the fluorescence quantum efficiencies are very much reduced.

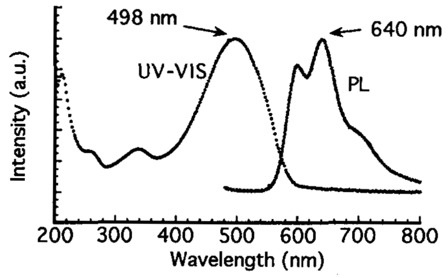


Figure 4. UV-VIS and PL emission spectra of films of BTEM-PPV **10**

Table 3. Characterization of polymers **9** and **10**

| Polymer | $\overline{M}_n$[a] (x $10^3$) | P.D. | Yield (%) | $\lambda_{max}$[b] (nm) | $PL_{max}$[b,c] (nm) | $E_R$[d] (V) | $E_O$[d] (V) |
|---|---|---|---|---|---|---|---|
| **9** | 47 | 9.0 | 25 | 494 | 601(0.6) | -1.35 | 0.5 |
| **10** | 41 | 3.7 | 31 | 498 | 640 (8.8) | -1.5 | 0.5 |
| MEH-PPV | - | - | - | 500 | 590 (15) | -1.8 | 0.47 |

[a] GPC in $CHCl_3$ using polystyrene as standards; [b] Measurements on thin films; [c] PL emission maximum (% efficiency given in parenthesis); [d] CV measurement conditions as described earlier, $E_R$ - reduction onset potential, $E_O$ - oxidation onset potential.

A LEC was fabricated using a blend of lithium triflate with the homopolymer **9**, and this device showed light emission at a low bias voltage (*ca.* 2.4 V), but at a low current density (Figure 5).

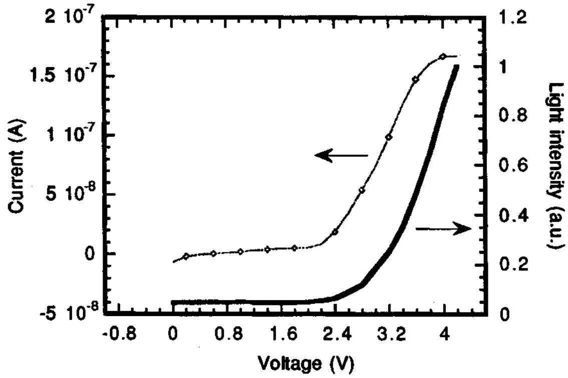


Figure 5. I-V-L characteristics of a LEC device fabricated using MTEM-PPV **9** with LiOTf

A single layer EL device was also fabricated with the related homopolymer BTEM-PPV **10** in order to evaluate the operating conditions in conventional polymer EL devices. The characteristics of this device are illustrated in Figure 6. We attribute the modest results with this material to the poor charge transporting properties of the device.

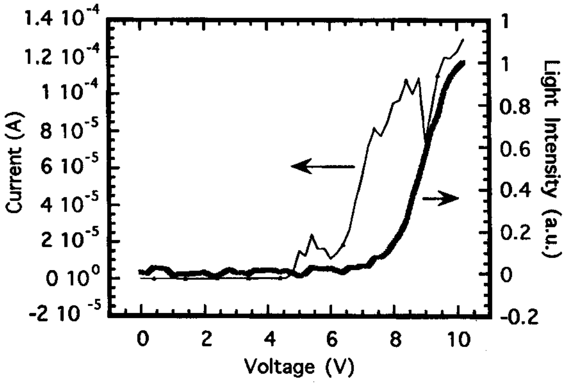


Figure 6. I-V-L characteristics of an EL device prepared using BTEM-PPV **10** in the configuration ITO/**10**/Al.

## EXPERIMENTAL

### Typical polymerization procedure for 9

*MTEM-PPV* **9** - To a stirred, degassed solution of NaH (60 % dispersion in mineral oil, 0.032 g, 0.81 mmol) in dry DMF (1 $cm^3$) was added all at once, a degassed solution of the bis(chloromethyl) precursor **8a** (0.1 g, 0.27 mmol) in dry DMF (1 $cm^3$) at room temperature. The reaction mixture was stirred at ambient temperature under a nitrogen atmosphere for 18 h and then poured into methanol (100 $cm^3$). The red precipitate was collected, redissolved in minimum $CHCl_3$ and reprecipitated into methanol (50 $cm^3$). The polymer was collected and dried *in vacuo* to afford the polymer **9** as a red solid (20 mg, 25 %). IR $\nu_{max}$ (film)/$cm^{-1}$ 2875, 1507 (Ar), 1208, 1108 (C-O), 967 (*trans*-vinylene PPV); $^1$H NMR $\delta_H$ (250 MHz; $CDCl_3$) 7.48 (1H, br m, conjugated unit), (1H, br m, conjugated unit), 4.25 (2H, br m, Ar-$OCH_2$), 3.95-3.88 (5H, br m, 2'$CH_2$ & Ar-$OCH_3$), 3.79-3.61 (6H, br m, 4'$CH_2$, 5'$CH_2$ & 7'$CH_2$), 3.58-3.53 (2H, br m, 8'$CH_2$), 3.34 (3H, br s, $CH_3$).

### Device Fabrication and Measurements

Single layer EL devices were fabricated by spin-coating the polymer on to standard ITO glass, followed by evaporation of an aluminum electrode on to the polymer (Ref. 24). For the LEC devices with the silyl polymer **1**, poly(ethylene oxide) and lithium triflate (50 % and 15 % w/w polymer respectively) were added into the chloroform solution. In the LEC device using polymer **9** only lithium triflate (*ca.* 7 % w/w) was used. The solutions were deposited as films onto ITO-coated glass substrates using a spin-coater at 2000-2500 rpm to obtain films of *ca.* 70-150 nm thickness. The aluminum electrode was deposited onto the polymer film surface by vacuum evaporation under a pressure of 7 x $10^{-6}$ mm Hg. The film thickness was measured with a Dektak-II surface profilometer. The active emissive area defined by the cathode was about 4 $mm^2$. The devices were fabricated in air, while the device measurements were carried out in vacuum (*ca.* 0.1 mm Hg). PL and EL spectra were recorded using a single-grating CCD spectrometer (Oriel Instaspec IV).

## CONCLUSION

In conclusion, we have shown that a variety of conjugated copolymers can be synthesized using the dehydrohalogenation route. The properties of the copolymers can be tuned according to composition. The homopolymer **1** has a very efficient photoluminescence and can be used in a LEC configuration to lower the turn-on voltage without significant compromise in device efficiency. On the other hand the homopolymers **9** and **10** were not as promising in the LEC configuration or a conventional device respectively, possibly owing to their poor charge transport properties. Future work will report the application of statistical copolymers based on the repeat units of **1** with **9** and **10**, respectively.

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