Our results show that the ferroelectric field effect can be achieved in high-quality epitaxial heterostructures. The main advantage of this integrated thin film approach is that the electric field necessary to switch the thin epitaxial PZT layer is only of the order of $10^5$ V $cm^{-1}$, which is an order of magnitude lower than what has been used for other field effect experiments performed on high-$T_c$ superconductors (*7*, *8*). As a result, the corresponding voltages are only a few volts (1 V per 1000 Å of PZT). Furthermore, the use of the nonvolatile polarization field from PZT allows us to rule out various concerns that have been raised with regard to field effect experiments on high-$T_c$ materials with ordinary dielectric insulators. For example, whereas such experiments attest to high-quality interfaces, the large fields that must be supplied across the dielectric during the measurement have caused concern about leakage current during measurement, heating effects, and electrostriction. Here, there was no voltage applied across the ferroelectric during transport measurements and hence no possibility of leakage currents through the ferroelectric compound or spurious resistive heating effects. Also, because the PZT has the same tetragonal crystal structure in its two polarization states, it is unlikely that strain is the source of the observed resistance change. Finally, we note that the choice of YBCO as the conductor in previous field effect experiments has raised the possibility that the effect is related to the motion of mobile O ions in the CuO chains, rather than to the response of the hole carriers to the applied electric field (*20*). In $SrCuO_2$, all the atoms are strongly bonded, and thus the observed resistance changes with applied electric field can arise only from changes in the free charge carrier density in the material.

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# Luminescence Enhancement by the Introduction of Disorder into Poly(*p*-phenylene vinylene)

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A method is described for increasing luminescence in poly(*p*-phenylene vinylene) (PPV) light-emitting diodes. Cis linkages were engineered into the PPV chain. These linkages interrupt conjugation and interfere with the packing of the polymer chains, which results in the formation of amorphous PPV. Large-area electroluminescent devices were prepared from this polymer. Devices made of an aluminum electrode, PPV as the luminescent layer, and an electron-transporting layer have internal quantum efficiencies of 2 percent, a turn-on voltage of 20 volts, and can carry current densities of 2000 milliamperes per square centimeter. The current density is at least an order of magnitude higher than previously obtained.

The potential for making large-area displays from easily processable polymers has driven much of the recent research in the area of polymeric light-emitting diodes (LEDs). Of all the polymers evaluated for LEDs, PPV has attracted the most interest. It is used in devices more than any other polymer as either the light-emitting layer (*1*, *2*) or the hole-transporting layer (*3*). PPV is commonly prepared by the Wessling precursor method that was developed some 30 years ago (*4*). We have previously shown that this method is laden with problems (*5*, *6*). The polyelectrolyte nature of the precursor leads to dramatic increases in viscosity during polymerization, which in turn limits yield. In addition, the polyelectrolyte is only soluble in polar solvents such as water or methanol, which are both poor solvents for spinning high-quality films. Large-area pinhole-free films necessary for displays are difficult to obtain by this method. The fact that the tetrahydrothiophenium group, used in the Wessling method, is an excellent leaving group further complicates this approach. This group is readily substituted with methoxy (*7*) and hydroxy (*8*) groups during polymerization and dialysis of the precursor. The hydroxy groups are then oxidized to carbonyls, which limit electroluminescence, when the precursor is thermally converted to PPV (*6*). Also, the extent of substitution can vary considerably with minor changes in the handling or storing of the precursor, resulting in dramatic differences in polymer performance. This extreme sensitivity to process variables makes the Wessling route to PPV unsatisfactory for manufacturing real devices. Another problem with the PPV produced by Wessling's method is that it is predominately trans and, therefore, is also highly crystalline.

Work by Yan *et al.* (*9*) indicates that photoluminescence efficiency can be increased in a polymer by separating the polymer chains. Reasoning that amorphous PPV would have better chain separation than crystalline PPV would, we devised a method to synthesize PPV in a way that would overcome most of the problems encountered in the Wessling route. Specifically, we wanted an organic soluble precursor to improve film quality and a leaving group that would not undergo nucleophilic substitution by hydroxyl groups and would be eliminated to produce a

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mixture of *cis*- and *trans*-PPV in order to reduce crystallinity.

To take advantage of the good hole-transporting properties of PPV and the advantages that an insoluble PPV layer offers in constructing bilayer devices, we chose to stay with a soluble precursor route to PPV. Our task was then to find an organic leaving group that would afford the precursor solubility in good spinning solvents and that could be thermally eliminated at elevated temperatures. These requirements led to a modification of the Wessling method in which a xanthate group would serve as both the base-catalyzed leaving group during precursor polymerization and as the thermally labile group during the conversion to PPV. The use of a xanthate group is an adaptation of the Chugaev reaction (*10*). We modified the reaction to lower the conversion temperature and to simplify monomer preparation. Literature on this reaction indicated that the thermal elimination should produce a PPV with a significant cis content (*11*). As pictured in Fig. 1, the cis linkages should disrupt conjugation and packing in PPV. This synthetic method is outlined in Scheme 1.

Monomer **I** was synthesized in one step and was found to be stable enough to store as a solid at room temperature without any sign of degradation or hydrolysis. The monomer was polymerized by dissolving it in tetrahydrofuran (THF) and then reacting it with potassium *tert*-butoxide at 0°C. The reaction appears to proceed via the quinoid intermediate, because the solution became red almost immediately upon addition of the base. The resulting precursor polymer **II** was completely soluble in common organic solvents such as THF, chloroform, 1,4-dioxane, toluene, and cyclohexanone. The weight-average molecular weight of the precursor was $\sim 6 \times 10^5$ with a polydispersity of 3.4, as determined by gel permeation chromatography (GPC) with polystyrene standards. This molecular weight is similar to that of the precursor polymer prepared by Wessling's method (*12*). There is, however, a second GPC peak at very low molecular weights, below 2000. We have not been able to separate this compound from the polymer even with reverse precipitation. But even with the low molecular weight impurity, PPV prepared by our method has superior properties to Wessling's PPV. According to infrared spectroscopic (IR) analysis, there was no sign of hydrolysis or elimination in the precursor.

The conversion of the precursor polymer was monitored by thermogravimetric analysis (TGA) and IR. TGA experiments showed that weight loss of the precursor polymer, presumably due to the elimination of the xanthic acid, started at 180°C (10°C/min heating rate under nitrogen). The IR spectra (Fig. 2) revealed that the precursor is not completely converted to PPV even at 250°C. The conversion process is thought to follow an elimination mechanism similar to that of the Chugaev reaction which is known to produce a mixture of cis and trans double bonds in solution through six-membered ring formation (*11*). The formation of *trans*-PPV is seen in the evolution of a peak in the IR spectrum at 962 $\mathrm{cm}^{-1}$ (Fig. 2), corresponding to the *trans*-vinylene C–H out-of-plane mode (*13*). This peak is the predominant peak in PPV prepared by Wessling's method. Our polymer also has a peak at 868 $\mathrm{cm}^{-1}$, which we assign to the formation of *cis*-PPV. We made this assignment based on the fact that *cis*-stilbene has a band at 862 $\mathrm{cm}^{-1}$ (*14*) and a copolymer of PPV and tetramethoxy PPV has a cis band at 882 $\mathrm{cm}^{-1}$ (*15*). In addition, this peak can be isomerized to trans by extended heating (6 hours) at 250°C after conversion at 180°C. The IR spectra of our PPV (**III**) are devoid of carbonyl peaks, as would be expected for a precursor free of hydroxy groups.

Despite the difference in conversion between samples heated to 180° and 250°C, the photoluminescence spectra of these samples are identical. Both have a peak maximum at 544 nm as compared with 549 nm for PPV synthesized by Wessling's method. This may be explained by the cis linkages which disrupt the conjugation in the polymer and, therefore, are the controlling factor in determining the conjugation length. Ultraviolet-visible (UVVIS) spectra of our PPV are also consistent with cis linkages. The peak maximum for our PPV converted at 225°C is blue-shifted by 27 nm with respect to the corresponding Wessling PPV. This is in agreement with trends reported for cis linkages in PPV oligomers (*16*). Electron diffraction of this new PPV revealed that it is amorphous irrespective of the conversion temperature. This is different from Wessling's PPV which yielded sharp and discrete crystallographic reflections (*17*). The amorphous nature of our polymer is in qualitative agreement with the presence of cis linkages.

We made single-layer LED devices by

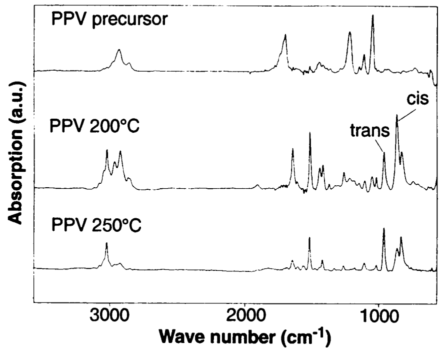


**Fig. 2.** IR spectra of the precursor polymer (top), PPV converted for 6 hours at 200°C (middle), and PPV converted for 6 hours at 250°C (bottom). a.u., arbitrary units.

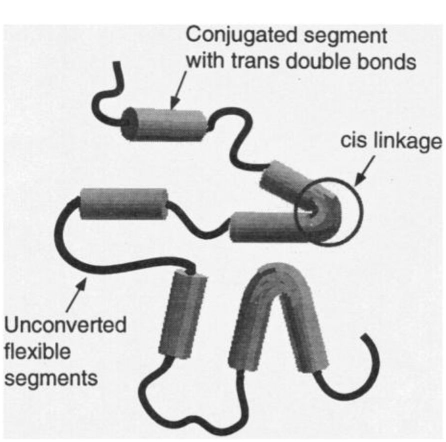
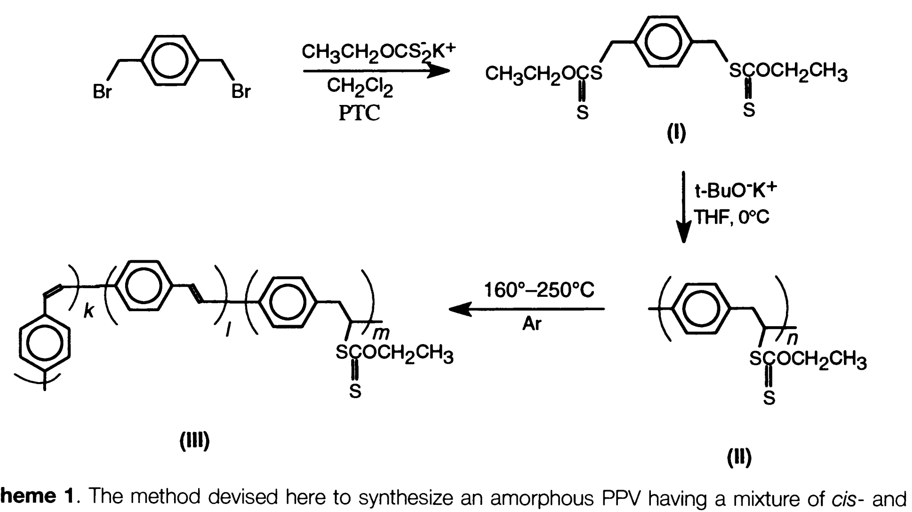


**Fig. 1.** Schematic diagram showing how cis linkages reduce conjugation and interfere with packing in PPV.



**Scheme 1**. The method devised here to synthesize an amorphous PPV having a mixture of *cis*- and *trans*-PPV.

spin-coating our precursor onto indium tin oxide (ITO)–coated glass, followed by thermal conversion to PPV at temperatures ranging from 160° to 250°C under a forming gas or an argon atmosphere. A 2000 Å thick layer of aluminum was then deposited on the PPV which had a thickness range of 700 to 1000 Å. We measured external quantum efficiencies by placing a silicon photodiode close to the device and measuring the light emitted with a Hewlett-Packard 4155 semiconductor parameter analyzer. The measurement was then corrected only for the photoresponse of the diode. The quantum efficiencies of these devices were independent of the conversion atmosphere. The quantum efficiencies for devices made from PPV converted at several temperatures are plotted in Fig. 3. Devices made with PPV converted at 170°C had the highest external quantum efficiency, 0.05% at 50 μA. This efficiency decreased with increasing conversion temperature, that is, higher xanthate elimination and higher trans content as determined by IR. Whereas we measure external quantum efficiency, the internal quantum efficiency of our devices is calculated with the assumptions put forth by researchers at Cambridge (*18*). Specifically, we multiply our external numbers by $2n^2$, where $n$ is the refractive index of glass. We use 1.5 for $n$ to be conservative in our efficiency calculations. With these assumptions, our internal quantum efficiency for a ITO-PPV-Al device is 0.22%. This is considerably higher than the 0.01% reported by Burroughes *et al.* (*1*) for a device prepared with Wessling's PPV.

According to photoluminescence and electroluminescence spectra, our PPVs converted between 180° and 250°C emit light with a wavelength of ~544 nm. When the conversion temperature was lowered to 170° or 160°C, the spectra shifted to 541 and 536 nm, respectively. Because the emission occurs from the longest chains (*19*), it is reasonable to speculate that the longest chain length of the thermally converted PPV depends on the conversion temperature below 180°C. Above 180°C, the longest chain length does not increase with increasing conversion temperature, probably because it is limited by the number of cis units. Because the highest electroluminescence efficiencies are obtained with partially converted PPV, it is important that the precursor polymer and partially converted PPV do not thermally eliminate at ambient temperature. This is not true for the polymer made by Wessling's method but it is true for our precursor.

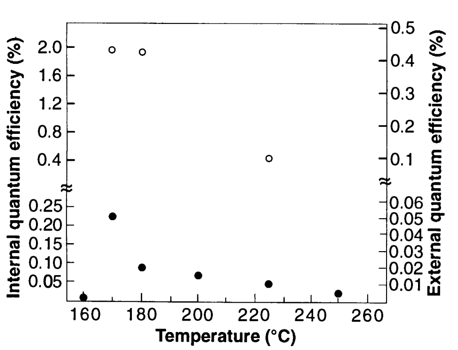


**Fig. 3.** Internal and external quantum efficiencies of LED devices made with PPV converted at various temperatures. Open circles represent devices made with an electron injection layer [ITO-PPV-(PBD + PMMA)-Al], and closed circles are for devices made with a single layer of PPV (ITO-PPV-Al).

Because electron-transporting layers are often used to increase device efficiency, we made some LEDs with a 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) in poly(methyl methacrylate) (PMMA) as a 300 Å layer between PPV and an aluminum electrode. These devices, made with PPV converted at 170° or 180°C, had an external quantum efficiency of 0.44%, presumably due to efficient electron injection and charge confinement (*20*). The internal quantum efficiency for these devices is 2% with a turn-on voltage of 20 V. Before our work the highest reported quantum efficiency for a double-layer device in which PPV was the luminescent layer was 1.0% with calcium as the electrode. Calcium increases the quantum efficiency of the device, as compared with aluminum, by at least a factor of five (*21*). Quantum efficiency data for all the conversion temperatures are summarized in Fig. 3. These data show that our PPV is different from PPV made by the Wessling method. The IR spectra of PPV **III** prepared by our method are devoid of carbonyl peaks as would be expected for a precursor free of hydroxyl groups. According to our previous experiments, the precursor polymer made by Wessling's method is susceptible to hydrolysis during synthesis and storage. The hydroxy groups are then converted to carbonyl defects during thermal conversion. Carbonyl groups were found to lower the photoluminescence and electroluminescence intensity. It seems unlikely, however, that the lack of carbonyl groups in our sample can account for all the improvement in efficiency. The enhancement is much larger than that seen in PPV made by the Wessling method, where we took extreme caution to obtain polymer which by IR was also free of carbonyls. Most of the increase is related to the fact that the cis linkages make our PPV amorphous. These data confirm the theory proposed by Yan *et al.* (*9*). That PPV converted at high temperature has lower efficiency also supports the importance of cis linkages. IR studies of these samples revealed that the cis content decreases as the conversion temperature increases (Fig. 2). Our data are also in agreement with other studies that claim that a polymer with a lower conjugation length has higher efficiency (*2*, *22*).

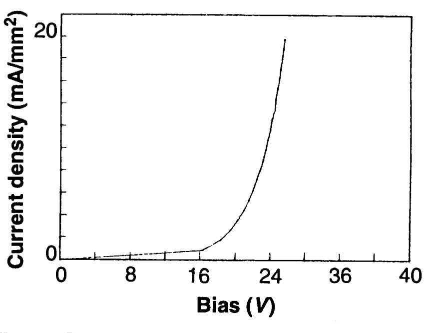


**Fig. 4.** Current versus voltage for a single-layer PPV LED with an aluminum electrode.

Because of the solubility of the precursor in good spinning solvents, we were also able to make large-area, 8-cm$^2$ devices with a single-layer configuration (ITO-PPV-Al). Green light emission ($\lambda_{max}$ from 542 to 546 nm) from the entire device provides evidence for the absence of pinholes which typically lead to device failure. Considering that fewer than 10% of the devices (with an active area of 1 mm$^2$) that we prepared with Wessling's PPV work successfully, the methodology reported here improves highly the quality of the PPV films. Moreover, LEDs prepared by our method can hold current densities of up to 2000 mA/cm$^2$ without electrical shorting (Fig. 4). This improvement may be attributed to film uniformity and the amorphous nature of PPV. Our synthetic method also consistently produced devices with identical quantum efficiencies, probably because of the chemical stability of the precursor.

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