Fluorinated Poly(*p*-phenylenevinylene) Copolymers: Preparation and Use in Light-Emitting Diodes

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A fluorinated poly(*p*-phenylenevinylene) analogue, *co*(TFPV-PV), has been prepared by copolymerization of fluorinated and nonfluorinated bissulfonium salt monomers. Conversion and yield decreased as a function of fluorine substitution. The UV−vis absorption was strongly shifted to the blue with increasing fluorine content. Complementary shifts in photoluminescence spectra were not observed, presumably because the fluorinated segments of the copolymer are very weakly luminescent relative to nonfluorinated segments. The photoluminescence spectra are therefore similar to those found for poly(*p*-phenylenevinylene) in the past. The *co*(TFPV-PV) compounds showed electroluminescence at an ac potential of ∼10 V (rms, 600 Hz) between ITO and Al electrodes. Maxima were shifted slightly to the blue with an increase in fluorine.

Introduction

In recent years there have been very significant changes in the way we look at the chemistry and physics of materials science. Whereas in the past, the technology of materials has almost entirely been based on inorganic compounds, the future appears to lie in the realization of the many properties and processing advantage of organic polymers. This trend is especially noticeable in the field of semiconducting and conducting materials based on highly conjugated organic polymers.[1] The interest in conjugated polymers stems from the understanding that their electrooptical properties, together with relatively simple device fabrication and flexible mechanical properties, offer great potential for application in a variety of devices.[2] One area of present attention has been connected with the use of conjugated polymers as organic light emitting diodes, LEDs. Thus, there have been many recent reports on the fabrication of polymer-based LEDs using multilayer heterostructures containing an emitter polymer sandwiched between conductive contacts with the proper work functions. Most research has been based on poly(*p*-phenylenevinylene), PPV, as the emitter. Common modifications include addition of substituents along the polymer chain for chemical control of the HOMO−LUMO bandgap with electron-donating and -withdrawing moieties[3]

and "geometric" control of the conjugation length by steric effects of the substituents.[4] Different electrooptical properties have also been achieved by variation of the aromatic moiety along the polymer chain by use, for example, of thiophenyl- and naphthyl-based conjugated polymers.[5] At present, it is clear that one of the major limiting factors in the commercialization of such polymer-based LED devices is their insufficient long-term stability. A few approaches have been espoused to increase long-term stability. For instance, one is the suggestion that self-assembly techniques for device preparation will increase stability,[6] another is that addition of polymeric electron-transport layers will yield longer living electroluminescent devices.[7] Furthermore, it has also been shown that application of ac instead of dc across the LED device increases the device lifetime.[8]

Another conceivable approach for increased longevity of LEDs concerns the preparation of emitter polymers which a priori have increased chemical stability toward degradation. One possible way to achieve such a goal is to replace the weaker carbon−hydrogen bonds by stronger and less reactive carbon−fluorine bonds in PPV so as to obtain a highly conjugated fluorinated polymer. Therefore, in this paper, we present our preparation of such fluorinated polymers and show our results concerning the absorption and emission properties of these fluorinated polymers.

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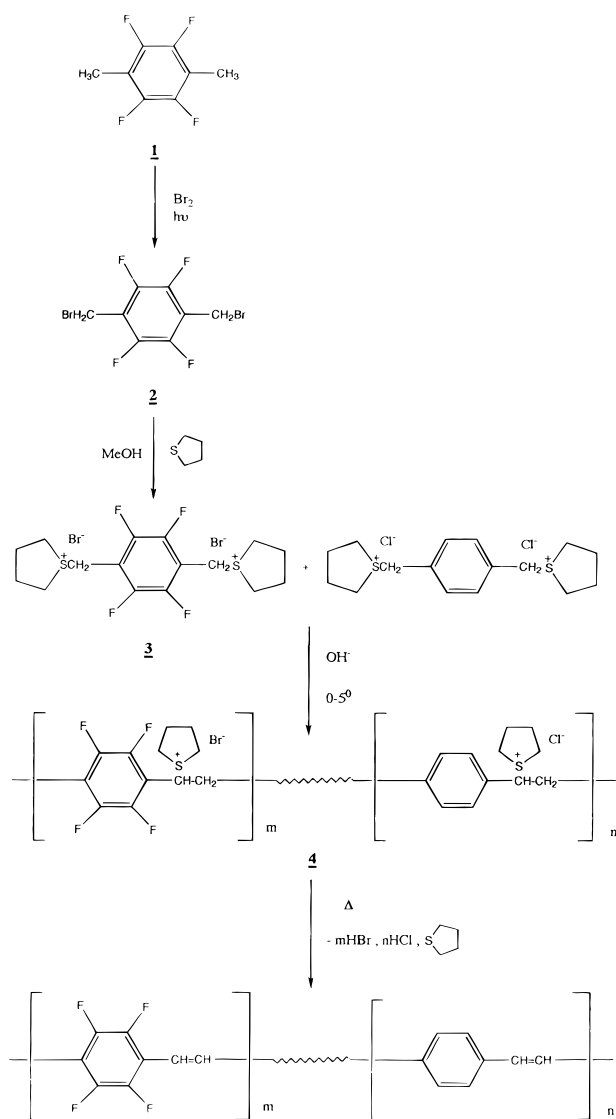
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Scheme 1. Synthetic Route to *co*(TFPV-PV)

Figure 1. Effectiveness of *co*(TFPV-PV) formation in terms of monomer conversion and polymer yield.

orinated monomer with NaOH and the mixture was dialyzed to remove low molecular weight oligomers (M_w < 12 000) and critically, polar impurities present in the solution. After dialysis the soluble precursor polymer was cast and the final conjugated polymer copoly(tetra-fluorophenylenevinylene−phenylenevinylene), *co*(TFPV-PV), was obtained by heating under vacuum. The monomer conversion to **4** and the final yield of *co*(TFPV-PV) as a function of the fluorinated monomer **3** is given in Figure 1. One clearly observes a decrease in both conversion and yield as more fluorinated monomer is used. Such phenomena have been observed in other copolymerizations of this type.[11] It is important to point out, however, that the ratios of initially mixed monomers are expressed in the final copolymer, *co*(TFPV-PV) in similar molar ratios. Thus, elementary analysis of a copolymer prepared from 20 mol % fluorinated and 80 mol % nonfluorinated monomer showed a de facto incorporation of 17 mol % fluorinated monomer.

Spectral Properties. The UV−vis absorption spectra of various *co*(TFPV-PV) polymers are shown in Figure 2. The strong blue shift of up to ∼60 nm as a function of fluorine content is clearly observed. This shift is explained as being a result of the inductive electron withdrawing properties of the fluorine substitution leading to reduced electron density in the conjugated polymer and leading to an increase in the HOMO−LUMO bandgap which is directly measured in the absorption spectra. On the other hand, in the photoluminescence spectra two observations are notable. First, as the fluorine content increases there is a significant decrease in the photoluminescence intensity of about 2 orders of magnitude when comparing 1% *co*(TFPV-PV) to 60% *co*(TFPV-PV). Second, as the fluorine content increases, there is very slight red shift, ∼5 nm, in the photoluminescence spectrum (Figure 3). This result was somewhat surprising considering the expected and observed significant blue shift in the UV−vis absorption spectrum. This result may be explained

Results and Discussion

Synthesis. The synthesis of fluorinated PPV analogues was carried out by adaptation of the known synthetic procedure developed by Wessling[9] and later by Lenz[10] for such polymers (Scheme 1). In this case, 1,4-dimethyl-2,3,5,6-tetrafluorobenzene, **1**, was brominated using molecular bromine to obtain 1,4-di-α-bromo)methyl-2,3,5,6-tetrafluorobenzene, **2**, in high yield. The bromomethyl compound was reacted with tetrahydrothiophene over 18 days in a methanol reflux to the required disubstituted sulfonium salt, **3**. This polar compound was isolated only approximately 80% pure. Since the polar impurities were identifiable with a high degree of certainty by combined use of ¹H NMR, ¹⁹F NMR, or fast atom bombardment mass spectra (FAB-MS, see Experimental Section), it is clear that in the next step the impurity(ies) neither was incorporated into the soluble precursor copolymer nor interfered with the polymerization reaction. The water-soluble sulfonium precursor copolymers, **4**, were prepared by mixing the required amounts of **3** and the analogous nonflu-
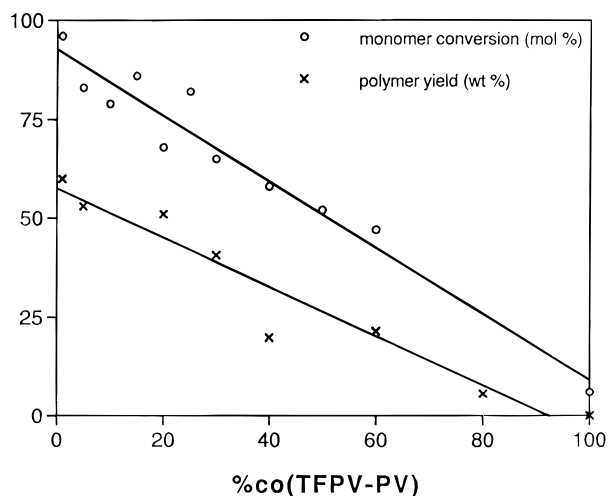
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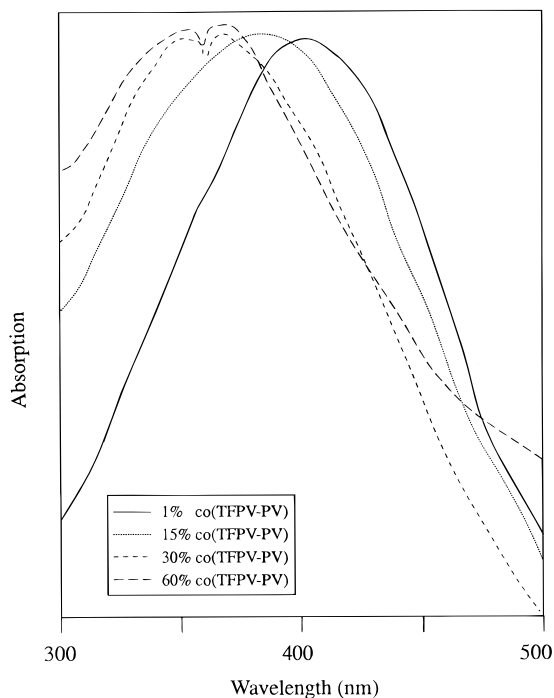
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Figure 2. UV−vis absorption spectra of *co*(TFPV-PV) copolymer films of ∼200 Å.
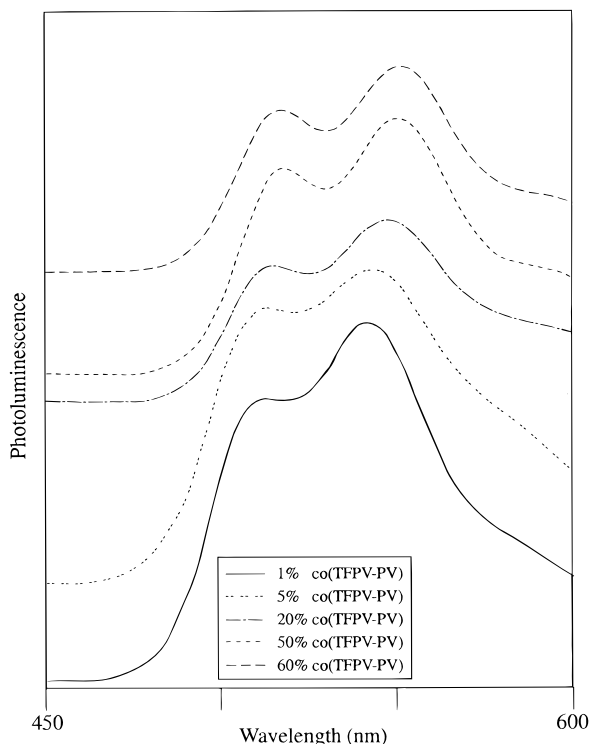

Figure 3. Photoluminescence spectra of *co*(TFPV-PV) copolymer films of ∼200 Å.

by the very weak photoluminescence of the terafluorophenyl derivative vs the phenyl derivative. The photoluminescence spectrum is dominated by the phenylenevinylene segments of the polymer. Thus, only at relatively low fluorine content, up to 20% *co*(TFPV-PV) is there a slight blue shift compared to PPV.[12]

The electroluminescence spectra of some of the co-(TFPV-PV) copolymer films (thicknesss 120 ± 10 Å) are presented in Figure 4. First it must be pointed out that application of dc voltage of up to 30 V did not yield any emission (beyond this potential cells were shorted) and
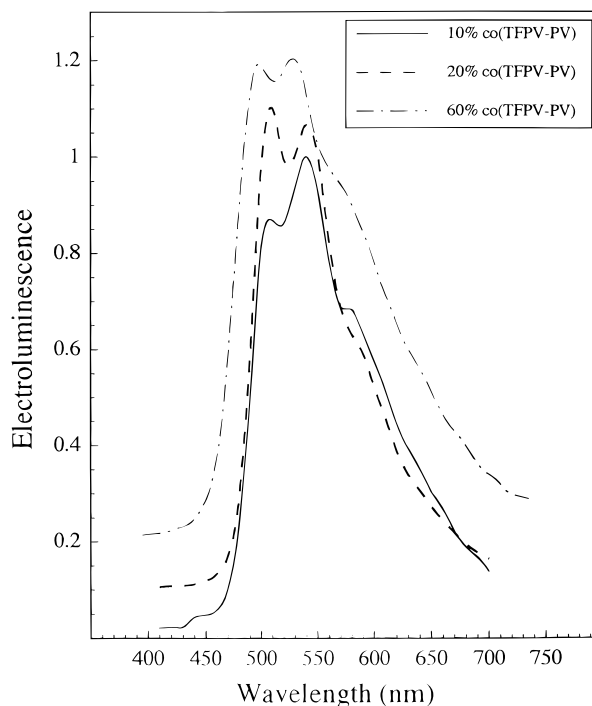

Figure 4. Electroluminescence spectra of *co*(TFPV-PV) copolymer films of ∼120 Å with ITO and Al contacts.

electroluminescence was measured by applying ac voltage (12 V, rms at 600 Hz). The electroluminescence spectra under these conditions showed a slight blue shift with increasing fluorine content. Thus, for 10% *co*-(TFPV-PV) the peak at 540 nm is stronger than that at 510 nm, whereas for 20% *co*(TFPV-PV) the situation is reversed and finally for 60% *co*(TFPV-PV) both peaks are shifted to 525 and 495 nm, respectively. This result shows that the electroemission efficiencies of the terafluorophenyl and the phenyl segments are of a similar order of magnitude and the electroluminescence spectra correspond more to those that may be expected from the HOMO−LUMO bandgap as viewed in the absorption spectra. Unfortunately, the threshold voltages for electroluminscence for *co*(TFPV-PV) are high compared to other conjugated polymers. This high threshold together with the weak luminescence properties made the study of LED stability with *co*(TFPV-PV) difficult.

Experimental Section

1,4-Di-α-bromomethyl-2,3,5,6-tetrafluorobenzene. 1,4-Di-α-bromomethyl-2,3,5,6-tetrafluorobenzene, **2**, was prepared according to the literature procedure[13] by adding dropwise over a period of 4 h, 6.15 mL (0.12 mol) of Br$_2$ to a refluxing solution of 10 g (0.056 mol) of 1,4-dimethyl-2,3,5,6-tetrafluorobenzene in 100 mL of CCl$_4$ illuminated by a 250 W tungsten lamp. The reaction was continued for another 2 h followed by removal of the CCl$_4$ by evaporation. The product was purified first by sublimation (50 °C at 1.5 mmHg) and then by recrystallization from ethanol; yield 77%; mp 68−70 °C. ^{1}H NMR in CDCl$_3$, quintet at 4.50 ppm; ^{19}F NMR in CDCl$_3$, quintet at −142.61 ppm.

1,4-(2,3,5,6-Tetrafluoro)phenylenedimethylene Bis-(tetramethylenesulfonium bromide), 3. Compound was prepared by reacting 14.5 g (0.043 mol) **2** and 22.8 mL (0.258 mol) tetrahydrothiophene (thiolane) in 150 mL of methanol at 50 °C for 18 days. The methanol was evaporated off under

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vacuum, 250 mL of acetone was added and the suspension stirred at 0–5 °C for 1 h. The crude product, 75% yield, was isolated by filtration. The FAB-MS using a magic bullet matrix, and ¹H NMR and ¹⁹F NMR in D₂O show that the desired compound is contaminated most probably by two compounds. The FAB-MS of **3** shows a peak at *m*/*z* 431, 433 (30) for M–Br and a base peak at 343, 345 (100) for M–Br–thiolane. Smaller peaks at intensities of ~20% at *m*/*z* 295, 383, 471 and 353, 441, 529 are attributed to a compound(s) with either one or no bromide anion (no ⁷⁹Br, ⁸¹Br pairs) and multiple thiolane substitutions since peaks are separated by an *m*/*z* of 88, the molecular weight of thiolane. Our explanation for the formation of this impurity(ies) centers around the substantial acidity of the benzylic hydrogen due to the nuclear substitution by fluorine. This acidity can lead to the non-base catalyzed elimination of hydrogen bromide and dimerization or oligomerization of the product remembering the polymerization reaction in the nonfluorinated substrates is base catalyzed and proceeds via HBr elimination. Elimination of hydrogen bromide can also lead to formation of a carbon–sulfur ylide which can react with excess thiolane leading to a dithiolane-substituted benzylic carbon. The presence of impurity(ies) complicates the unambiguous analysis of the ¹H NMR; however, the peaks (ppm) at 3.96 singlet, 3.60, 3.48 quintets, and 2.40 overlapping multiplets are attributed to the benzylic hydrogens, and those α and β to sulfur in thiolane, respectively. The presence of fluorine in the nuclear ring brings about differentiation of chemical shifts because the most stable conformation of the product allows for significantly different hydrogen-fluorine distances for the two types of α- and β-hydrogens. Additional thiolane units are observed at 3.27 (triplet) and 1.92 (quintet) and 2.69 (triplet) and 1.85 (quintet). Correlation between the various thiolane hydrogens was based on 2D Cosy measurements. The ¹⁹F NMR of **3** has a singlet at −142.09, and the impuriy(ies) have peaks at 138.28 and 139.99. The purity, ~80%, has been estimated from the integration of the ¹⁹F NMR peaks.

Formation of Water-Soluble Sulfonium Precursor Copolymers, 4. The water-soluble precursor copolymers were prepared by adding 0.2 mol of 1 N NaOH to a mixture of a total of 0.2 mol at the required ratios of 1,4-(2,3,5,6-tetrafluoro)phenylenedimethylene bis(tetramethylenesulfonium bromide) and 1,4-phenylenedimethylene bis(tetramethylenesulfonium chloride) in 75 mL of distilled water under nitrogen at 0–5 °C. The mixture was stirred vigorously for 3 h and the excess base neutralized using 1 N HCl. The amount of acid used in the titration served also to compute the monomer conversion in the polymerization. The copolymers were thoroughly purified by dialysis, at least ten times, at 4 °C using a 12 000 M_w cellulose membrane.

Formation of Conjugated *co*(TFPV-PV). The purified precursor copolymers were spin cast on a cleansed quartz substrate (UV−vis and photoluminescence) or ITO (electroluminescence) and heated under 10^{-6} Torr at 220 °C for 12 h to form films of *co*(TFPV-PV) required for the spectral analyses. Films were weighed to compute the total yield of *co*(TFPV-PV). Films were also analyzed for fluorine content; thus the nominally 20% *co*(TFPV-PV) yielded 11.16% F translating to 17% *co*(TFPV-PV).

Spectral Measurements. UV−vis absorption spectra were measured on a Hewlett-Packard HP8452A diode array spectrometer. PL spectra were recorded on a JASCO spectrofluorimeter (FP-770), excitation was at the absorption peak, typically 375 nm. EL spectra of films of a thickness of 120 ± 10 Å were recorded at a 10−12 V potential ac at 600 Hz using an Oriel monochromator, and the light intensity was measured with a photomultiplier tube (Products for Research Inc. Model R955).

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