*Macromolecules* **2001,** *34,* 6117−6120

# Synthesis and Characterization of Poly(2,3,5,6-tetrafluorophenylenevinylene): A Revisit

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*Received September 25, 2000; Revised Manuscript Received May 1, 2001*

ABSTRACT: 1,4-Di-α-bromomethyl-2,3,5,6-tetrafluorobenzene **(1)** was prepared from the bromination of 2,3,5,6-tetrafluoro-*p*-xylene. The product was carefully purified and analyzed by GC/MS, HPLC, FTIR, and $^1$H NMR. The structure of **1** was unequivocally confirmed by the X-ray diffraction method. The melting point of 126 °C for **1** was vastly different from the previously reported value of 68−70 °C. Poly(2,3,5,6-tetrafluorophenylenevinylene) (PTFPV) homopolymer was successfully prepared via the bromine precursor route (BPR). The polymer showed excellent photoluminescence with emission maxima at shorter wavelengths of 485 and 515 nm. The single-layer device of ITO/PTFPV/Al configuration emitted green light at low turn-on voltage of about 4.2 V. The results demonstrated that PTFPV prepared via BPR was a good emitting material for the LEDs in the green-blue region.

## Introduction

Poly(1,4-phenylenevinylene) (PPV) and its derivatives (PPVs) are promising new materials for polymeric light-emitting diodes (LEDs).[1−4] Different types of substituents on the phenylene ring or on the vinylene of the conjugated polymers and the effective conjugated lengths can cause significant differences in the electronic structures, which in turn affect the electrical−optical properties of the polymers.[5−7] There has been considerable interest in fluorine-substituted PPVs due primarily to their expected better chemical stability.[8−11] In addition, the electron-withdrawing property of the fluorine atom is expected to cause spectra shift for the PL and EL. More recently, OLEDs fabricated by using perfluorinated phenylene dendrimers have been reported.[12] Interestingly, some fluorine-substituted PPVs have been reported to show contrasting direction in spectra shift. For example, the electronic spectrum of poly(2-fluoro-1,4-phenylenevinylene), a monofluorine-substituted PPV, is very similar to that of PPV, with hardly any spectrum shift. On the other hand, the emission spectra of 2,5-difluoro PPVs, such as poly(2,5-difluoro-1,4-phenylenevinylene) and poly(2[5]-(*n*-hexyloxy)-5[2]-fluoro-1,4-phenylenevinylene), are red-shifted considerably compared to that of PPV.[11] These fluorine-subsituted PPVs have turn-on voltage varying from 4 to 30 V. Benjamin et al.[10] have reported the synthesis of copolymers of 2,3,5,6-tetrafluorophenylenevinylene (TFPV) and PV by the Wessling method. The conjugated copolymers have relatively high turn-on voltages and weak PL and EL properties. No studies were done on the poly(2,3,5,6-tetrafluorophenylenevinylene) (PTFPV) homopolymer which was reported to be difficult to obtain by the Wessling method.[10] In this paper, we report the synthesis of PTFPV homopolymer via the BPR method. The starting compound synthesized via a modified bromination method had a vastly different melting point from that reported by Benjamin et al.[10] The PTFPV homopolymer prepared in this study shows good PL and EL properties.

## Experimental Section

**Materials.** All chemicals were used as received without further purification unless specified otherwise.

**Characterization.** The NMR spectra were recorded by a Bruker Avance-400 MHz Fourier transform spectrometer. Infrared spectra were recorded by a Perkin-Elmer 1725-X Fourier transform infrared (FTIR) spectrometer. The melting points were determined by a differential scanning calorimeter DSC-7 apparatus (Perkin-Elmer) at a heating rate of 20 °C/min. GC/MS spectra were recorded on a QCQ (Finnigan) (ionization mode EI = 70, column 30 m × 0.25 mm × 0.25 $\mu$m, liquid-phase DB-5MS, column temperature from 50 to 250 °C at a rate of 8 °C/min). HPLC analysis was performed using a $C_{18}$ reverse-phase column (STR ODS-II, 4.6 mm × 150 mm) and a SPD-M10Avp UV detector (Shimadzu) at 240 nm with $CH_3OH/H_2O$ (8:7, v/v) mixture as eluant and a flow rate of 1.2 mL/min. Elemental analysis was performed using a CHN-LECO 600 instrument. Intrinsic viscosity [$\eta$] was determined in chloroform at 30 °C with a Cannon Ubbelohde dilution viscometer. UV−vis absorption was recorded on a HP8452 spectrophotometer (Hewlett-Packard), and the photoluminescence spectra were measured on a Flwinlab LS50B luminescence spectrophotometer (Perkin-Elmer).

**X-ray Diffraction.** The crystallographic data were collected on a single crystal using a Siemens P4 X-ray diffractometer with Mo Kα radiation by the $\theta/2\theta$ scan.[13] The intensity data were reduced and corrected for Lorentz, polarization, and extinction factors. Absorption correction was applied based on psi-scan using the applied program. The crystal structure was solved by using the direct method and refined with full-matrix least-squares on $F^2$ (computing data collection, Siemens XSCANS; computing cell refinement, Siemens XSCANS; computing data reduction, Siemens SHELXTL; computing structure solution, SHELXS-86; computing structure refinement, SHELXL-93; computing molecular graphics, Siemens SHELXTL).[14]

**Synthesis.** The synthetic route for the starting compound and PTFPV is shown in Scheme 1.

**Synthesis of 1,4-Di-α-bromomethyl-2,3,5,6-tetrafluorobenzene (1).** Compound **1** was prepared via a modified method similar to the literature procedure.[10] Into a refluxing solution containing 10 g (0.056 mol) of 2,3,5,6-tetrafluoro-*p*-xylene in 100 mL of $CCl_4$, 6.15 mL (0.12 mol) of $Br_2$ was added dropwise over a period of 4 h. The solution was constantly illuminated by two 250 W tungsten lamps during the addition process. The reaction was continued for another 2 h after which $CCl_4$ was partially removed by rotary evaporation. The con-

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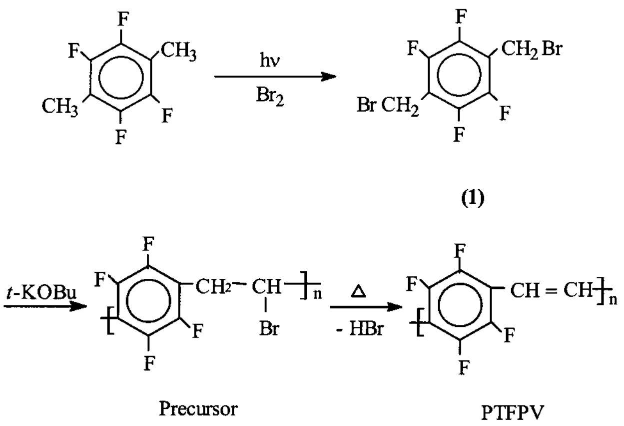
**Scheme 1. Synthesis Route of PTFPV**



centrated solution was then placed in a refrigerator overnight. The white precipitate formed was removed by filtration. The solid was then washed with 30 mL of saturated $Na_2CO_3$ aqueous solution, followed by distilled water three times. The white solid product was purified by recrystallization from ethanol three times. The final crystalline product had a melting point of 126 °C. The yield of purified product was 6.82 g (36.1%). Elemental analysis: C, 28.62%; H, 1.23%; F, 23.38%; Br, 46.81%. Calculated: C, 28.61%; H, 1.20%; F, 22.62%; Br, 47.57%. $^1H$ NMR in $CDCl_3$: a sharp singlet (width at half-height < 3.2 Hz) at 4.53 ppm.

**Precursor of PTFPV.** Compound **1** (2.90 g, 0.0086 mol) was dissolved in 100 mL of THF. A freshly prepared THF solution of potassium *tert*-butoxide (*t*-BuOK) (28 mL, 0.3 M) was added slowly over a period of 30 min. The mixture was stirred for another 2 h at room temperature. The resultant solution was viscous and yellow in color. The solution was then added to methanol for precipitation. The yellow precipitate was redissolved in 50 mL of THF and was purified in distilled water by dialysis at room temperature using a 12 000 $M_w$ cutoff cellulose membrane for 3 days. The precipitate formed was filtered off and dried in a vacuum oven at room temperature for 24 h. The yield of the purified product was 0.41 g (18.7%). Elemental analysis: C, 35.9%; H, 1.27%. Calculated: C, 37.65%; H, 1.18%. Intrinsic viscosity $[\eta] = 1.46$ dL/g (30 °C, chloroform).

**Final Conjugated PTFPV.** The purified PTFPV precursor was dissolved in chloroform solution and cast onto a cleansed quarts substrate, followed by heating in a vacuum oven at 210 °C for 4 h to form PTFPV polymer film. Elemental analysis: C, 55.0%; H, 1.17%. Calculated, C, 55.2%; H, 1.15%.

## Results and Discussion

**Characterization of 1.** Because of the fact that the melting point of **1** was found to be 126 °C, which is vastly different from that reported by Benjamin et al.,[10] the product was carefully analyzed by various methods. The FTIR spectrum of **1** is shown in Figure 1. The absorption at 600 $cm^{-1}$ due to the $CH_2$–Br stretch band is clearly present, while the $CH_3$ peak around 1380 $cm^{-1}$ is absent, indicating the two $CH_3$ groups in the starting material 2,3,5,6-tetrabromo-*p*-xylene have been brominated to $CH_2$–Br. The $^1H$ NMR spectrum shows a sharp single resonance peak at 4.53 ppm attributed to the two methylene protons of $CH_2Br$. This is in variant with the $^1H$ NMR data of Benjamin et al., who have reported a quintet at 4.50 ppm for compound **1** in $CDCl_3$, but no coupling constants are reported. This is rather surprising as compound **1** is not expected to give rise to a quintet. The four aromatic fluorine atoms are not all magnetically equivalent to the two benzyl protons. If at all there is any coupling between the aromatic fluorine and the $-CH_2-$ protons, one might expect a triplet or just a multiplet. However, the sharp single peak with the peak width at half-height < 3.2 Hz obtained from our NMR analysis clearly shows that there is no coupling effect.

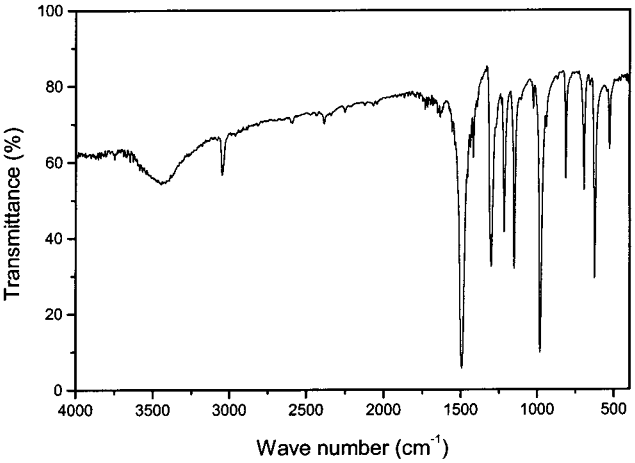


**Figure 1.** IR spectrum of **1** in KBr disk.

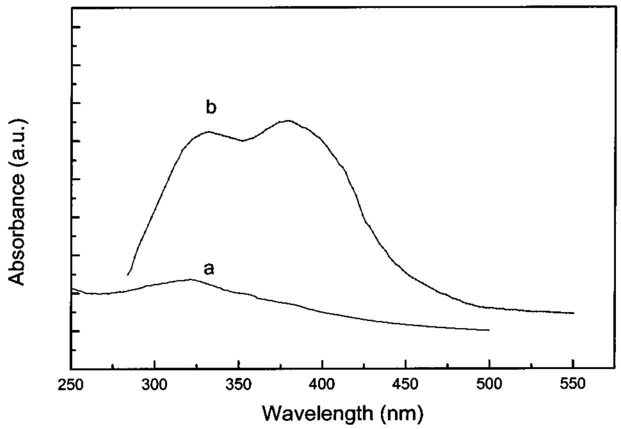


**Figure 2.** UV–vis absorption spectra of (a) PTFPV precursor and (b) PTFPV (after heating the precursor at 210 °C for 4 h).

The HPLC chromatogram has only one component, indicating that the compound is indeed pure. The GC-MS analysis of compound **1** showed a single GC single peak at a retention time of 12.52 min, and the MS has peaks at *m*/*e* of 336, 255, and 176, agreeing well with the structure of **1**.

**Characterization and PL Properties of PTFPV.** The absorption spectra of the polymer precursor and conjugated polymer converted by heating are shown in Figure 2. The FTIR of the final conjugated polymer of PTFPV is shown in Figures 3. The peaks of 973 $cm^{-1}$ (*trans*-vinylene C–H) and 624 $cm^{-1}$ (*cis*-vinylene C–H), indicating that both the *trans*-vinylene C–H and *cis*-vinylene C–H structures are present. Figure 4 shows the PL spectra of PTFPV with two excitation wavelengths at 350 and 380 nm. The PL spectrum shows two broad peaks with maxima at around 465 and 500 nm and a shoulder at around 440 nm. The feature of this spectrum is similar to those of poly((2-fluoro-1,4-phenylenevinylene)[11] and PPVs.[15,16] The multipeak feature of the PL spectrum may indicate the possible presence of more than one chromophoric component or the species exist in multiple chromophoric environments.[17] While it is also possible that the PL spectrum could be complicated by the presence of trace amounts of unconverted precursor, such unconverted residues have been

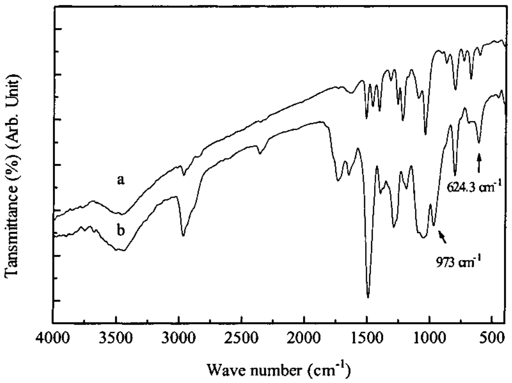
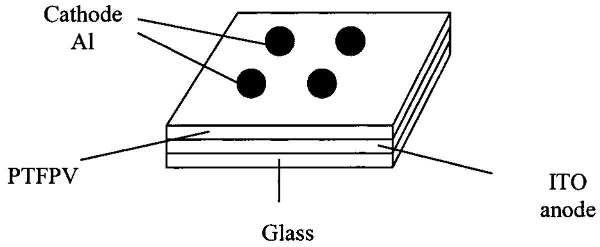


**Figure 3.** FTIR spectra of (a) PTFPV precursor and (b) PTFPV (after heating the precursor at 210 °C for 4 h).

**Scheme 2. Structure of ITO/PTFPV/Al LED**



found to have little effect on the emission wavelength.[11] The fact that the PL spectra were relatively unaffected by the excitation wavelength from 320 to 400 nm also suggests that the polymer is reasonably pure.

**Electroluminescent Properties of LEDs.** An indium tin oxide (ITO)-coated glass with electrical resistance of 60 Ω was cleaned by sonication and acetone and then dried in a vacuum at room temperature for 4 h. An LED consisting of a PTFPV layer sandwiched directly between ITO (positive contact) and an aluminum layer (negative contact) was fabricated as shown in Scheme 2. A thin film of PTFPV was formed on ITO glass by spin-coating using 20 mg/mL solution in chloroform at 1500 rpm. After evacuation for 8 h at room temperature to eliminate the residual solvent, the film was heated at 210 °C for 4 h under a $N_2$ atmosphere. The treated film was then placed in a desiccator and dried for 8 h under vacuum. This was followed by vapor deposition of aluminum through a mask (3 mm in diameter) at a chamber pressure of at least $5 \times 10^{-6}$ Torr. The top electrode Al was evaporated onto the polymer in a JEOL JEE-400 vacuum evaporator at a rate of 2−5 Å/s. The thickness of the Al was about 1000 Å. A typical LED was 3 mm in diameter. The effective area of the LED was $7.07 \times 10^{-2}$ cm$^2$.

Basic electrical characterizations involved measuring the device current and light output as a function of applied voltage. A HP 6282A or a HP 6212B dc power supply supplied the voltage across the device. The current was measured by a HIOKI 3256 digital hitester. For the simultaneous measurement of the total integrated light output, a silicon photodiode (RS 303-674, 1.00 cm$^2$ active area) was placed right below the active light emitting in the forward direction. The photodiode was significantly larger than the operating device ($7.07 \times 10^{-2}$ cm$^2$) and thus could collect all the light emitted in the forward direction. The distance between the device and photodiode was kept as small as possible. The photodiode was used under zero bias, and the generated current and light output was measured simultaneously. The diodes were driven with direct current. The device characteristics were measured in air at ambient temperature.

For the photodiode instrument used, the emitting light intensity efficiency ($\gamma_I$) is related to the emitting maximum ($\lambda$) by the following equation:

$$\gamma_I = 0.2 + 8.1968 \times 10^{-4}(\lambda - 450) \quad (\text{mA/mW})$$

Hence, for the device fabricated by using PTFPV having an emitting maximum at 485 nm, the values of $\gamma_I$ calculated are 0.2287 mA/mW. Emitting light power ($P$) can be calculated from the detected light current ($I$) by the following equation: $P$ (mW) = $I/\gamma_I$.

The emitted green light could be easily observed by the naked eye for all the single-layer devices fabricated. Figure 5 shows that the turn-on voltage of the ITO/PTFPV/Al single device is about 4.2 V. This is similar to the single-layer device fabricated by using poly(2[5]-(*n*-hexyloxy)-5[2]-fluoro-1,4-phenylenevinylene).[11]

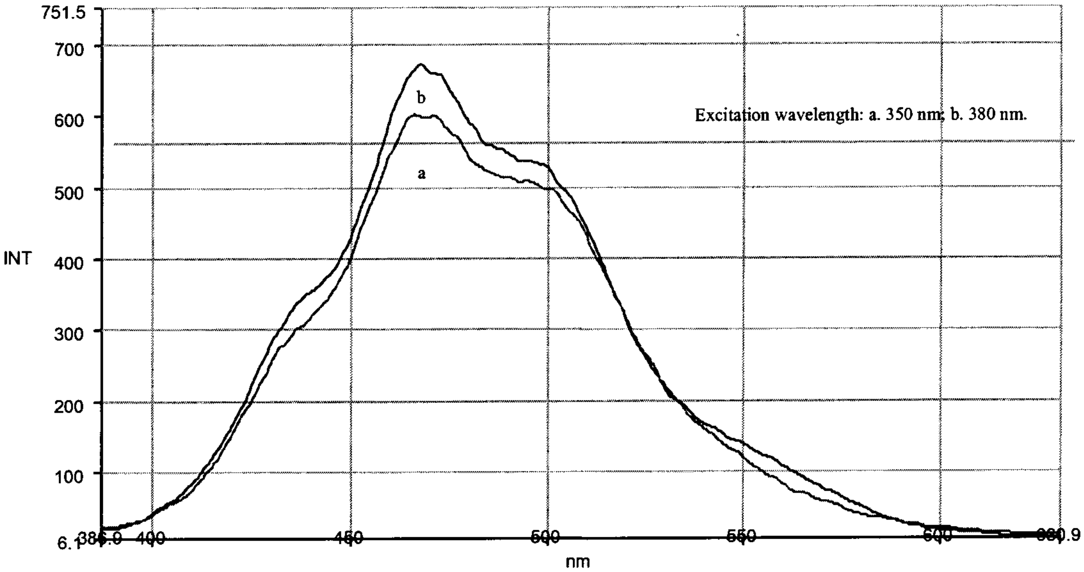


**Figure 4.** Photoluminescence spectra of PTFPV film on glass.

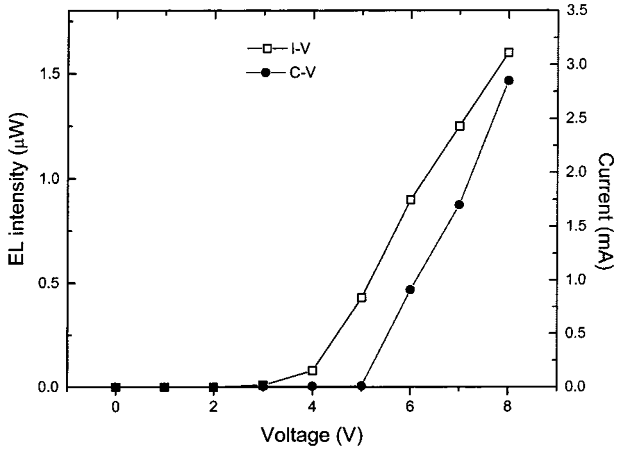


**Figure 5.** *I*−*V* and *C*−*V* curves of PTFPV.

## Conclusion

Compound **1** synthesized in this study had been carefully characterized by several analytical techniques. The compound was unequivocally confirmed to be indeed 1,4-di-α-bromomethyl-2,3,5,6-tetrafluorobenzene by an X-ray crystallographic study. The melting point of 126 °C for compound **1** was substantially higher than that of 68−70 °C reported by Benjamin et al.[10] It is unclear why the two values could be so vastly different. PTFPV homopolymer could be prepared by the BPR method. The single-layer LED with the ITO/PTFPV/Al configuration emitted blue light with low turn-on voltage of about 4.2 V.

**Acknowledgment.** This research was funded by the Academic Fund, National Institute of Education, Nanyang Technological University, Singapore, RP15/99GLH. Y.M.W. thanks NTU for the research Grant ARC 1/97GLH and research scholarship.

**Supporting Information Available:** X-ray structure of **1**, packing arrangements in the unit cell viewed along *a* and *b* axes, and table of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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