Blue Electroluminescence from Poly(*p*-phenylene) Solubilized by Perfluoropropylation

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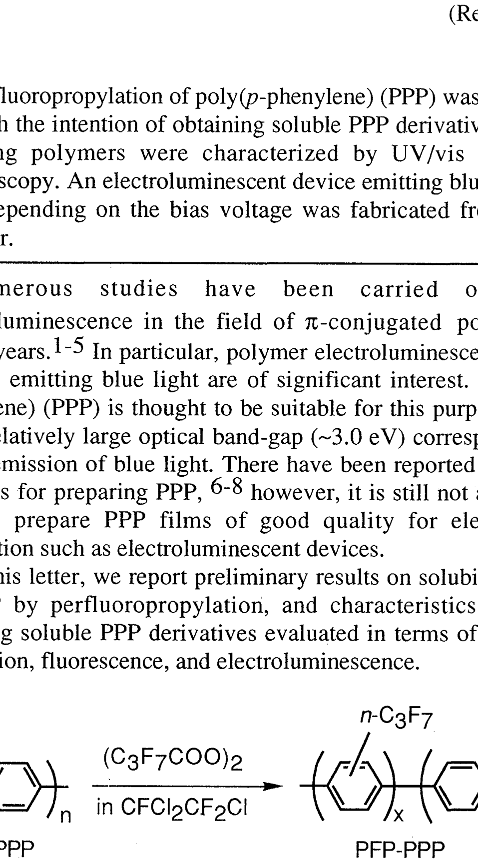
Perfluoropropylation of poly(*p*-phenylene) (PPP) was carried out with the intention of obtaining soluble PPP derivatives. The resulting polymers were characterized by UV/vis and IR spectroscopy. An electroluminescent device emitting blue-green light depending on the bias voltage was fabricated from this polymer.

Numerous studies have been carried out on electroluminescence in the field of π-conjugated polymers recent years.[1-5] In particular, polymer electroluminescent (EL) devices emitting blue light are of significant interest. Poly(*p*-phenylene) (PPP) is thought to be suitable for this purpose due to its relatively large optical band-gap (~3.0 eV) corresponding to the emission of blue light. There have been reported several methods for preparing PPP, [6-8] however, it is still not a trivial task to prepare PPP films of good quality for electronic application such as electroluminescent devices.

In this letter, we report preliminary results on solubilization of PPP by perfluoropropylation, and characteristics of the resulting soluble PPP derivatives evaluated in terms of optical absorption, fluorescence, and electroluminescence.



PPP used as the starting polymer was synthesized by coupling of Grignard reagents of *p*-dibromobenzene according to the literature.[8] PPP was perfluoropropylated with bis(perfluorobutyryl) peroxide by the following procedure.[9,10] PPP (0.50 g, 6.6 mmol monomer unit) dispersed in 1,1,2-trichlorotrifluoroethane (70 g) was added to 1,1,2-trichlorotrifluoroethane solution (30 g) containing bis(perfluorobutyryl) peroxide (3.24 g, 7.6 mmol) in nitrogen atmosphere. The mixture was stirred at 45 °C for 5 h, and then extracted with chloroform. The extract solution was evaporated, washed repeatedly with methanol, and dried to afford perfluoropropylated PPP (PFP-PPP). Insoluble polymeric material was also recovered by filtration, and purified in a similar manner. The yield of the soluble fraction was 60 wt%.

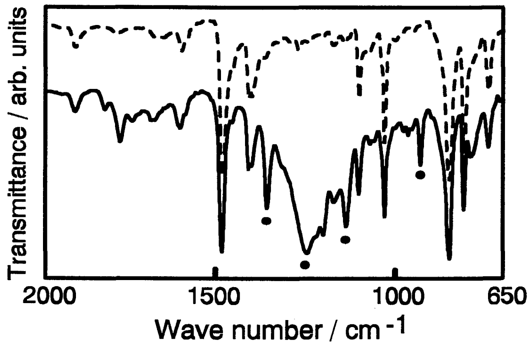


Figure 1. FT-IR spectra of PPP (dotted line) and soluble fraction of PFP-PPP (solid line). Spectra were displaced for clarity. Dots show the peaks ascribed to perfluoroalkyl groups.

Figure 1 shows FT-IR spectra of the starting PPP and the soluble fraction of PFP-PPP recorded on a Jasco 300E FT-IR spectrometer. The principal difference between the two samples was that strong peaks of fluoroalkyl groups ($-CF_2-$ and $-CF_3$) appeared between 1350 and 1100 cm^{-1} in the latter. The IR spectrum of the insoluble fraction of PFP-PPP was basically the same as that of the soluble fraction. The IR spectra also indicate that introduction of perfluoropropyl groups is a replacement reaction with aromatic hydrogens, and the main chain structure of PPP was not seriously changed. Elemental compositions of the samples are shown in Table 1. Determination of halogen content was not available, however assuming all the heteroatoms in the starting PPP are from bromine, and they terminate both ends of the molecule, we obtain an averaged molecular formula, $Br(C_6H_{4.3})_{13.3}Br$, i.e. degree of polymerization of about thirteen. If we assume that all the heteroatoms in the resulting polymers are bromine and fluorine, and aromatic hydrogens are substituted by perfluoropropyl groups, the number of perfluoropropyl group introduced to PPP was estimated to be 1.9-2.3 and 1.5-1.6 per molecule (i.e. thirteen benzene rings) for the soluble and insoluble fractions of PFP-PPP, respectively, from carbon and hydrogen balance. Thus, the soluble fraction of PFP-PPP is considered to carry a larger number of perfluoropropyl groups than the insoluble fraction, which presumably governs the solubility of the molecules.

Table 1. Elemental compositions of the polymers

Sample	C	H	N	Others[a] (%)
PPP	81.5	4.9	N.D.[b]	13.6
Sol. PFP-PPP	66.8	3.7	N.D.	29.5
Insol. PFP-PPP	70.2	3.9	N.D.	25.9

[a]100-(C+H+N)%. [b]Not detected.

Figure 2 shows UV/vis absorption spectrum of PFP-PPP film prepared by spin coating from a tetrahydrofuran solution. The band gap energy of this polymer was estimated to be 3.5 eV from the analysis of the absorption edge with a plot of ($h\nu$) vs. $(\alpha h\nu)^2$, where α, h, and ν are absorbance, Plank's constant and frequency of light, respectively. A photoluminescence spectrum

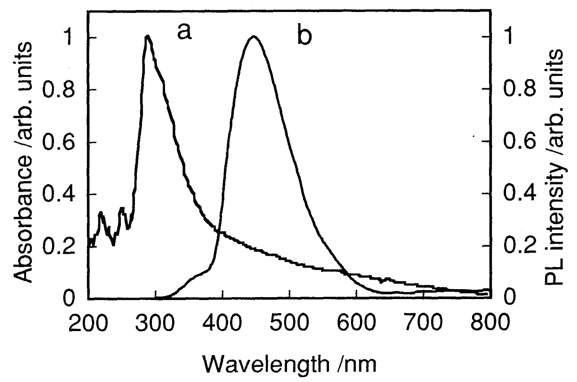


Figure 2. UV/vis absorption (curve a) and photoluminescence (curve b) spectra of a soluble PFP-PPP. Excitation wavelength was 300 nm.

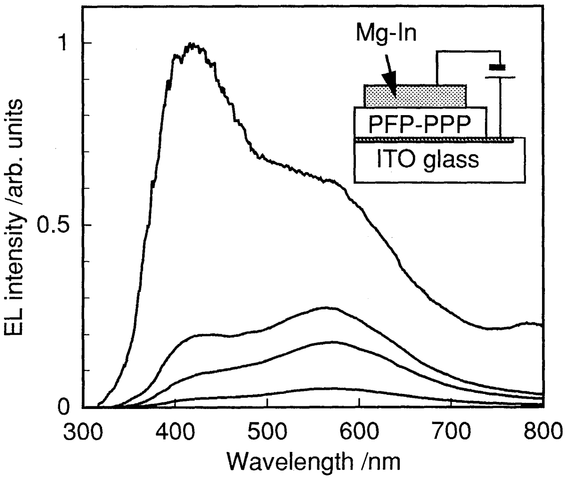


Figure 3. EL spectra of a device comprising PFP-PPP layer. Bias voltage applied on the ITO electrode was 9, 18, 24, and 30 V for the curves from the bottom to the top, respectively. Inset shows the schematic of the device.

of the film is also shown in Figure 2, indicating that the photoluminescence peak is located at 450 nm corresponding to the photon energy of 2.8 eV. Thus, it is considered that emission from exciton and/or exciton-polaron states rather than the interband emission is predominant. Comparing the band-gap (E_g) of PFP-PPP with those of unsubstituted PPP reported in the literature, the introduction of perfluoropropyl groups in PPP resulted in the increase of Eg. Namely, E_g of PPP prepared by precursor polymer route[11] and by electrochemical polymerization[12] or vacuum deposition[13] are reported to be 2.7 and 3.0 eV, respectively. A possible cause for the increase of the E_g of PFP-PPP is the electron withdrawing nature of perfluoropropyl group. However, it is more likely that the steric effect of perfluoropropyl group is predominant: perfluoropropyl group interferes with the coplanar configuration of phenylene rings in PPP backbone, which decreases the effective conjugation length in PPP main chain. The latter explanation is supported by the fact that the increase of E_g to a similar magnitude was also observed in PPP with electron donating substituents such as poly(2,5-diheptyloxy-*p*-phenylene)[14] and alkyl-substituted PPP copolymer.[15] In addition, the ionization potential (5.7 eV) of PFP-PPP evaluated by cyclic voltammetry agreed well with that of poly(2,5-diheptyloxy-*p*-phenylene).[14]

EL spectra of a device comprising PFP-PPP layer sandwiched between indium-tin oxide (positive contact)-coated quartz plate and a magnesium-indium thin layer (negative contact) are shown in Figure 3. The thickness of the polymer was estimated to be 140 nm from optical absorption, and the device was operated at liquid nitrogen temperature. It can be seen that the emission peak shifted to larger energy side of the spectrum with increase of the bias voltage. The color of the emission changed from green to blue with increase of the bias voltage. The EL spectrum obtained at 30V was quite similar with the photoluminescence spectrum shown in Figure 2 except a slight blue-shift of the emission peak and more pronounced emission at longer wavelength region. The reason for the change of the EL spectra with bias voltage is not clear at the moment, however emission from some defect states with smaller energy level may be predominant at small bias voltage (i.e. small current) region.

In summary, we have succeeded in obtaining a soluble derivative of PPP by perfluoropropylation of PPP with bis(perfluorobutyryl) peroxide. The resulting polymer was found to carry 1.9-2.3 perfluoropropyl group per averaged molecule consisting of about thirteen benzene rings from elemental analysis, and provided thin films of good quality by spin coating. E_g of PPP increased with the introduction of perfluoropropyl group, which was ascribed to the steric effect of the substituent. Blue to green light-emission depending on the electric bias was observed from an EL device based on PFP-PPP. It was suggested that pefluoroalkylation presented here provides a convenient way to convert highly aromatic insoluble polymers into a soluble and processible form.

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