Synthesis and Properties of Multifunctional Poly(2-trimethylsilyl-1,4-phenylenevinylene): a Novel, Silicon-substituted, Soluble PPV Derivative

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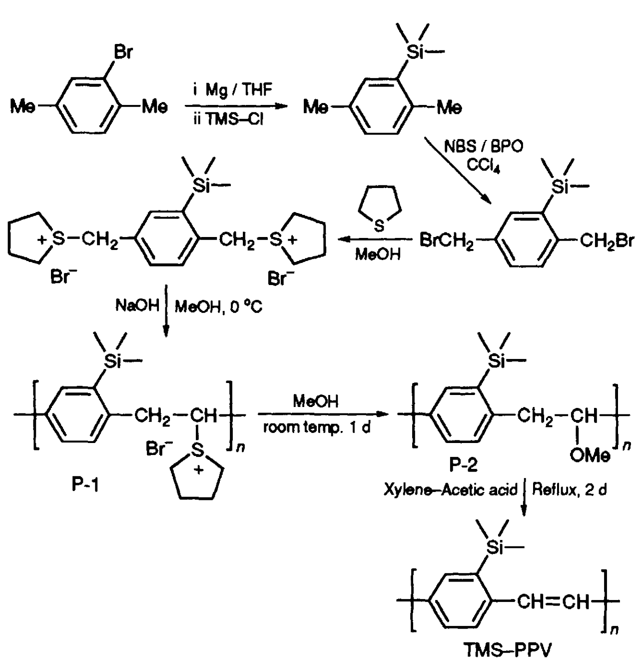
The novel, silicon-substituted, soluble PPV derivative, poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS–PPV), is prepared in a solution elimination process and shows high electrical conductivity after I_2 doping, high third-order nonlinear susceptibility and green light-emitting properties.

Poly(1,4-phenylenevinylene) (PPV) and its derivatives have possible applications in electronic and photonic devices.[1] Recently, Hoger *et al.* reported the synthesis of a novel, silicon-substituted PPV derivative, poly[2-(3-*epi*-cholestanol)-5-(dimethylthexylsilyl)-1,4-phenylenevinylene], and demonstrated that the presence of silicon enlarges the semiconductor band gap.[2] The synthesis and characterization of silicon-substituted PPV derivatives have also been presented previously.[3,4] Properties and processability of PPV derivatives have improved recently. Here, we report the synthesis and properties of the soluble, silicon-substituted, PPV derivative, poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS–PPV).



Scheme 1 The synthetic route of soluble TMS–PPV through solution elimination process

As shown in Scheme 1, water-soluble precursor polymer, P-1, was converted to the organic-soluble precursor polymer, P-2, in methanol. GPC measurement of this polymer with poly(styrene) as the calibration standard showed a weight average molecular mass of 185000 and polydispersity of 2.0. TMS–PPV was obtained through solution elimination in xylene and acetic acid, similarly to the method of Wudl *et al.*[5]

TMS–PPV shows an absorption maximum and band edge at 420 and 510 nm, respectively. These results are slightly blue-shifted compared with those of unsubstituted PPV (426, 530 nm),[6] presumably because the bulky TMS slightly breaks the coplanarity of the conjugated backbone.[2].

The electrical conductivity of TMS–PPV was measured by the four-probe method at room temp. The electrical conductivity of I_2 doped TMS–PPV was 2×10^{-2} S cm^{-1}. This result shows a great contrast to the fact that the unsubstituted PPV cannot be doped with the same dopant.[7]

TMS effectively breaks the dense packing structure of PPV, so facilitating the approach of dopant and leading to oxidation of the conjugated polymer backbone, thus TMS–PPV can be easily doped with a weak oxidizing dopant like I_2.

The third-order nonlinear susceptibility, $\chi^{(3)}$ ($-\omega;\omega,\omega,-\omega$), of TMS–PPV was determined by the degenerate four-wave mixing (DFWM) technique using 400 fs laser pulses at 602 nm. The calculated $\chi^{(3)}$ value was 3.3×10^{-10} esu and this is similar to that for unsubstituted PPV of 4.0×10^{-10} esu at the same wavelength reported previously.[8] Silicon thus has a similar influence on third-order nonlinear optical effects to that of hydrogen.

The photoluminescence (PL) spectrum was observed at room temp. utilizing a lock-in amplifier system with a chopping frequency of 150 Hz and an Ar ion laser (457.9 nm) as an excitation light source. Fig. 1 shows the PL spectrum of TMS–PPV. This is similar to that of PPV and three well-defined equally spaced phonon sidebands appear at 510, 550 and 590 nm, consistent with a stretching vibration of the carbon–carbon backbone. The peak at 510 nm is stronger than that at 550 nm, the opposite is observed for PPV.[9] This can be explained by the relaxation of the excited state to the different vibrational levels of ground state. The EL device was made with ITO and aluminium as anode and cathode, respectively, and TMS–PPV showed bright green electroluminescence.

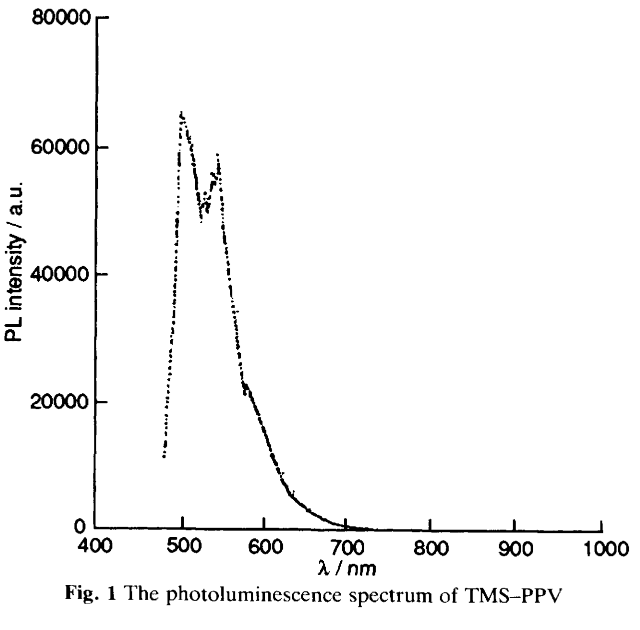


Fig. 1 The photoluminescence spectrum of TMS–PPV

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