# A New Synthetic Route to Polyheteroarenediylvinylenes

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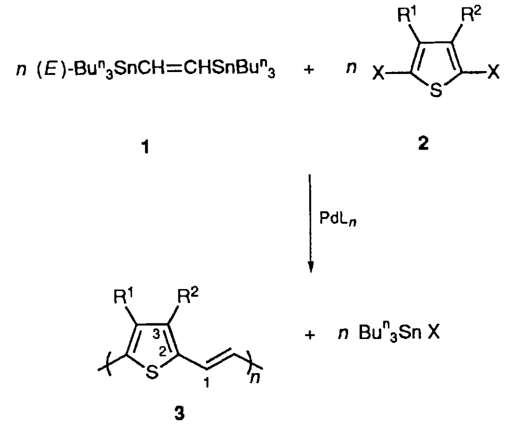
The cross coupling reaction of dihalogenoheteroaromatic compounds and 1,2-bistributylstannylethylene catalysed by palladium phosphine complexes is found to provide a new simple route to conducting polyheteroarenediylvinylenes.

Polyarenediylvinylenes and polyheteroarenediylvinylenes are presently being investigated extensively in view of their interesting electrooptical properties.[1] These materials are mainly prepared through the thermal decomposition of a precursor polymer.[1,2] Recently a nickel catalysed coupling of Grignard derivatives of substituted thiophenes and 1,2-dichloroethylene has been reported.[3,4] We propose now a method of general applicability which can lead in a single step to polyconjugated systems. We have found that the C–C cross coupling reaction of α, α′-dihalogeno heteroaromatic compounds and 1,2-bistributylstannylethylene **1** catalysed by Pd complexes is a convenient route to polyheteroarenediylvinylenes. This reaction is an extension of the Pd catalysed cross coupling of monohalogenoaromatic and organotin compounds.[5] As an example Scheme 1 shows the preparation of some poly(thiophene-2,5-diylvinylenes) **3**.

In a typical catalytic reaction compound **1** (1 mmol) and **2** (1 mmol) were reacted in presence of a mixture of $[\{(\eta^3\text{-}C_4H_7)Pd(OAc)\}_2]$ (0.025 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (0.1 mmol) in boiling dimethylformamide (DMF). Product **3** separated from the reaction mixture as a



a; X = Br; $R^1 = R^2 = H$
b; X = I; $R^1$ = n-decyl; $R^2$ = H
c; X = I; $R^1 = R^2 = Bu^n$

**Scheme 1**

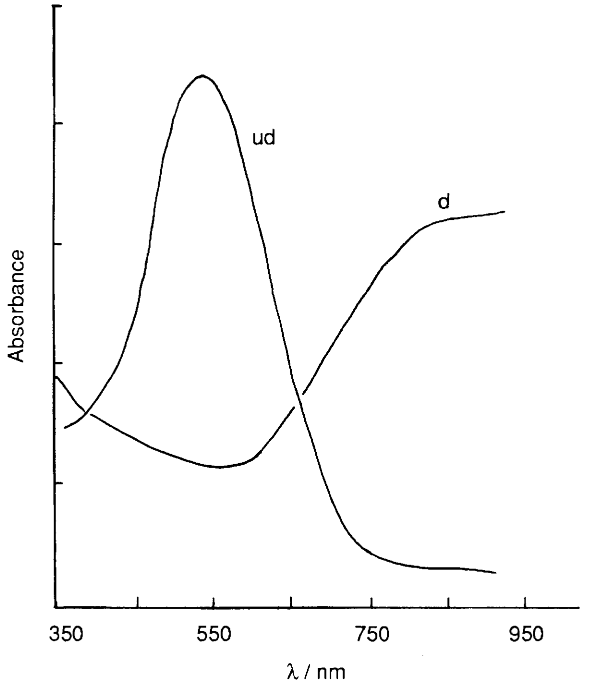
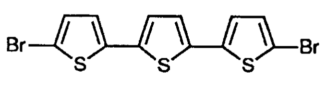


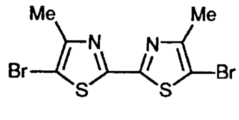
**Fig. 1** *In situ* absorption spectra of **3c** cast on ITO glass: ud, undoped; d, doped

black powder (yield *ca.* 50%). Polymer **3a** was insoluble, while **3b** and **3c** were soluble in common organic solvents. GPC analysis of **3b** showed a bimodal distribution of molecular weight centred at 12 900 and 6000 (referenced to a polystyrene standard). While the $^{13}C$ NMR spectrum of **3b** is rather complex owing to the irregularity in the head to tail attachment of the thienyl group in the polymer backbone, the spectrum of **3c** is fully consistent with the structure in Scheme 1 [$\delta$ ($CDCl_3$) 119.4 (C-1), 141.6, 135.3 (C-2 and C-3) and 33.5, 26.8, 22.8 and 13.9 ($Bu^n$)]. The absorption at 920 $cm^{-1}$ in the IR spectrum of **3** indicates a *trans*-geometry for the vinyl group.[2]

The absorption maximum for the $\pi$–$\pi^*$ transition of polymer **3a** is at 530 nm (solid state, KBr pellet in transmission) while films cast from chloroform solution of **3b** and **3c**



**4**



**5**

show maxima at 600 and 570 nm respectively. The $E_g$ value, calculated by extrapolation of the absorption edge, is 1.7 eV for both polymers **3b** and **3c**. Films from chloroform solutions of **3b** and **3c** were cast on transparent indium tin oxide glass (ITO) and were electrochemically doped under nitrogen in acetonitrile solution containing $Bu^t_4NClO_4$ (using Pt as counterelectrode). Both the polymers show an electrochromic effect in the visible spectral region. The *in situ* spectra of polymer **3c** in the doped and undoped state are shown in Fig. 1. The film of the insulating material is blue while the polymer in the oxidized state is transparent and its absorption maximum is shifted to wavelengths higher than 800 nm. The electrochemical doping process is not completely reversible. Doping and undoping cycles of **3b** and **3c** result in a decrease of the intensity of the band due to the $\pi$–$\pi^*$ transition together with a shift towards higher energy. Conductivity measurements in iodine-doped powders after compression showed values close to $10^{-2}$ S $cm^{-1}$.

The above polymerization reaction has been successfully extended to the heteroaromatic halides **4** and **5** (results will be reported elsewhere) and is currently being exploited for the preparation of conducting polymers which were not previously easily accessible.

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