Synthesis of Aryl Substituted Polyphenylenevinylenes by $W(CO)_6$ mediated Desulphurisation–Polymerisation of Bisdithiolanes

Chi Hong Kuo and Tien-Yau Luh*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Treatment of bis(ethylene dithioacetal) derivatives of *para*-dibenzoylbenzenes with $W(CO)_6$ in refluxing chlorobenzene gives aryl substituted polyphenylene vinylenes in good yields.

The fabrication of polymers having conjugated systems has received much attention owing to the potential application of these materials.[1] For example, polyphenylenevinylenes (PPVs) have been shown to have conductive properties.[2] Relatively little attention has been paid to the chemistry of substituted PPVs.[3] We recently found that dithiolanes can undergo inter- and intra-molecular desulphurisation–dimerisation leading to carbon–carbon double bond formation.[4] The reaction gave particularly high yields when diaryldithiolanes were employed as the substrates. We now report the first application of this newly discovered reaction in the synthesis of aryl substituted PPVs.

Treatment of terephthaldehyde with aryl Grignard reagents followed by oxidation with Jones reagent, or MnO_2 yielded the corresponding diketones (**1a**—**c**).† Bisdithiolanes (**2**)† were prepared in excellent yields from the reaction of ethane-1,2-dithiol and (**1**) in the presence of $BF_3{\cdot}OEt_2$. A mixture of (**2**) and $W(CO)_6$ (3 mol equiv.) in chlorobenzene was heated under reflux for 2—3 days. After being cooled to room temperature, the solvent was removed and the residue was triturated with ethyl acetate. The soluble portion was evaporated and the residue was chromatographed on silica gel to give a yellowish solid, which was pyrolysed at 250 °C for 1 h to yield the reddish brown solid (**3**). The results are summarized in the Table 1. Average molecular weights determined by gel permeation suggest that these polymers have 6 to 14 repeating phenylenevinylene units.

Elemental analyses of (**3a**—**c**) showed that (**3a**) and (**3b**) are essentially hydrocarbons and (**3c**) is mainly a methoxy substituted hydrocarbon. In other words, compounds (**3**) either have high molecular weights or the terminal dithiolane

Table 1.

Polymer	% Yield	$\bar{M}_n$	T_g/°C	T_m/°C
(**3a**)	56	3400	130	253
(**3b**)	64	3600	114	250
(**3c**)	61	1900	92	254[a]

[a] Determined by thermomechanical analysis.

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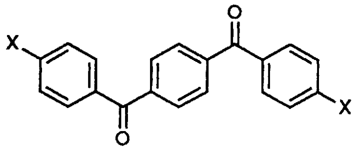
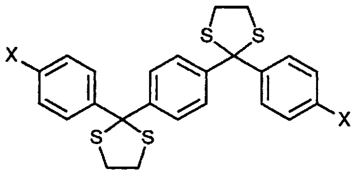
† All new compounds gave satisfactory spectroscopic results (NMR, IR, MS), and elemental analyses.



(1)



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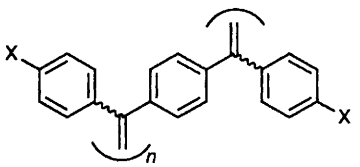

(3)

a; X = H
b; X = Me
c; X = MeO

function may have reacted further under the reaction conditions. The ^{1}H NMR spectra of (**3a**—**c**) showed high-field signals (*ca.* δ 3.8), which may be ascribed to the residual dithiolane functions at the terminal units of the polymers. In comparison with the average molecular weights of these polymers determined by gel permeation, the intensity of these high-field resonances relative to those in the aromatic region is low. This observation, however, is compatible with the elemental analytical data which also indicated that the terminal dithiolane functions may not survive under the reaction conditions. Thus, further reaction may occur, but not lead to the extension of the chain length which results in increasing molecular weight.

The mode of the $W(CO)_6$ mediated reductive coupling of dithiolanes has recently been investigated.[4d] Evidence suggested that the reaction proceeds *via* a radical fragmentation[5] to give a thioketone intermediate which may then couple to yield the alkene.[4d] This mechanism would be applicable to the polymerisation reaction, and it seems likely that the terminal dithiolane group may have reacted further under the reaction conditions.

Thermogravimetric analyses (TGA) curves showed that a significant weight loss of the polymers (**3a**—**c**) occurred at *ca.* 500 °C. Differential scanning calorimetry (DSC) indicated that (**3a**—**c**) give similar melting temperature (T_m). Interestingly, the glass transition temperatures (T_g) decrease with increasing electron-donating ability of the substituent on the aromatic ring.

In summary, we have demonstrated a new methodology for the synthesis of polyconjugated PPVs. The extension of this reaction to other polymer synthesis is in progress.

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