Poly-1,4-diketones obtained by the Stetter Reaction: a New Route to Conducting Heterocyclic Polymers

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The electrically conducting, alternating copolymers *para*-phenylene-2,5-pyrrole and *para*-phenylene-2,5-thiophene were prepared by the Stetter reaction followed by ring closure and subsequent doping with I_2 or AsF_5.

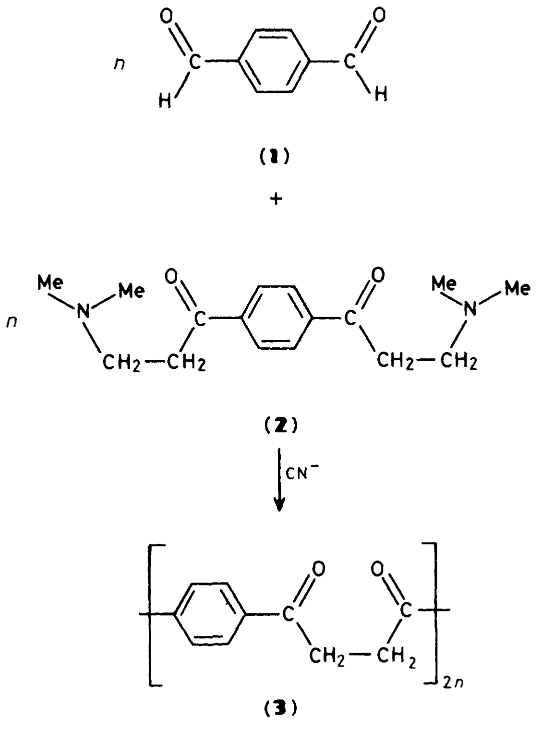
Recently the design of new synthetic routes to conducting polymers has received much interest.[1] The most remarkable results have been obtained for polyacetylene,[2] resulting in excellent conductivities and a reasonable processability. For heterocyclic polymers, all syntheses known today are based on the coupling of pyrrole or thiophene monomers, either electrochemically[3] or by $FeCl_3$ oxidation of pyrrole,[4] or by Grignard-type reactions of 2,5-dibromo-thiophene.[5] To date no schemes have been proposed in which the heterocycle is formed in a reaction performed on a preformed polymer. This is surprising, since the synthesis of pyrroles and thiophenes by ring closure of the appropriate precursor is a well-known reaction.[6] The reason that this procedure has never been used in polymer chemistry is probably due to the lack of useful precursor polymers. In this paper we describe the synthesis of such a precursor by a new polymerization and the subsequent reactions leading to electrically conducting polymers (Scheme 1).

For the synthesis of the precursor polymer we made use of the Stetter reaction.[7] Poly-1,4-phenylenebutane-1′,4′-dione (**3**) was formed in the reaction of terephthalic-dicarboxaldehyde (**1**) and the bis-Mannich base of 1,4-diacetylbenzene (**2**). This reaction was carried out in dimethylformamide (DMF) using a catalytic amount of NaCN. After the formation of the deep-red-coloured cyanohydrin anion, the reaction mixture became very viscous and finally a light-yellow polymer precipitated. In order to remove low molecular species the polymer was washed thoroughly with a variety of solvents, leading to (**3**) in 81% yield. All spectroscopic data are in agreement with the proposed structure.† Molecular weight determination of the polymer was hampered by the insolubility of (**3**) in all common solvents. With CPMAS ^{13}C n.m.r. spectroscopy no resonances for the expected end groups were detected, (Scheme 2).

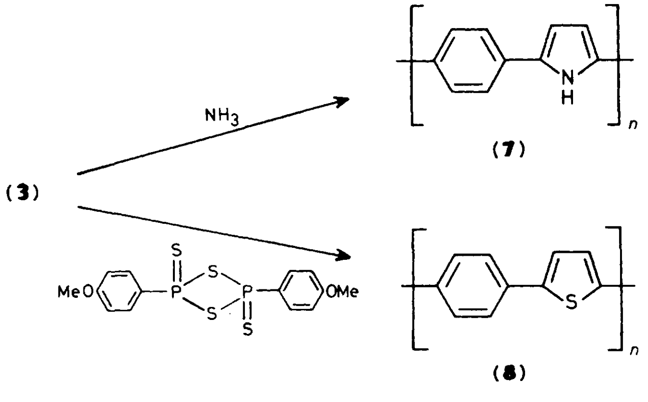
This new condensation polymerization represents the first example of a polymerization using the Stetter reaction. Since a large variety of aromatic aldehydes and Mannich bases undergo the Stetter reaction, a broad scope for this new polymerization is foreseen.

Before performing the heterocyclic ring closure on polymer (**3**), we studied the formation of 2,5-diphenylpyrrole (**5**) and 2,5-diphenylthiophene (**6**) from 1,4-diphenylbutane-1,4-dione (**4**). Both (**5**) and (**6**) were isolated in quantitative yield from the mild reaction of (**4**) with ammonium acetate and Lawesson's reagent, respectively.‡ For the conversion of polymer (**3**) into the alternating copolymers (**7**) and (**8**) more severe reaction conditions were required. The results from the synthesis of these polyaromatics are given in Table 1 and Figure 1. Although in both cases all the carbonyl groups of (**3**) were converted eventually [see Figure 1(d) and (f)] F.T.-i.r. spectra indicated that some imine intermediate remained from the heterogeneous reaction with ammonia [Figure 1(d)].

Upon doping with I_2 or AsF_5 both polymers (**7**) and (**8**)



Scheme 1



Scheme 2

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† *Selected spectroscopic data* for (**3**): m.p. >250 °C; i.r. (KBr): 1680, 841 cm^{-1}, c.p.m.a.s. ^{13}C n.m.r.: δ 32.4, 129.4, 138.5, 197.5.

‡ *Selected spectroscopic data* for (**5**): m.p. 140—141 °C (lit. 143—144 °C, Beilstein 20, IV, p. 4152); i.r. (KBr): 3458 cm^{-1}; ^{1}H n.m.r. (Me_2SO) δ 6.6, 7.0—8.0, 11.2. For (**6**): m.p. 151—154 °C (lit. 150—155 °C, Beilstein 17, IV, p. 686); i.r. (KBr): 688, 750, 805 cm^{-1}; ^{1}H n.m.r. (Me_2SO) δ 7.2—7.9.

Table 1. Ring closure of (**3**) and conductivity of (**7**) and (**8**).

Reaction conditions[a]	I.r.[b]	Doping[c]	Conductivity[d]/S cm^{-1}
(**3**) + liq. NH_4Ac (125 °C; 48 h)	(b)		
(**3**) + NH_3 (150 °C; 9 bar; 16 h)	(c)		
(**3**) + NH_3 (250 °C; 9 bar; 16 h)	(d)	(**7**) + I_2 (100 °C)	0.1
(**3**) + L.r. (chlorobenzene; 131 °C, 48 h)	(e)		
(**3**) + L.r. (dichlorobenzene; 190 °C, 48 h)	(f)	(**8**) + I_2 (100 °C)	0.03
(**3**) + L.r. (dichlorobenzene; 190 °C, 48 h)	(f)	(**8**) + AsF_5 (room temp.)	0.01
(**8**) (by Grignard, ref. 8)		(**8**) + I_2 (80 °C)	10^{-6}

[a] Reaction conditions to convert (**3**) into (**7**) and (**8**), L.r. = Lawesson's reagent. [b] The notations refer to the i.r. spectra of the polymers produced, as given in Figure 1. [c] The doping of the polymers (**7**) and (**8**) is performed using iodine vapour or AsF_5 at room temperature and at a pressure of 500 Torr (1 Torr = 133.322 Pa). [d] Conductivities as measured with the four probe method.

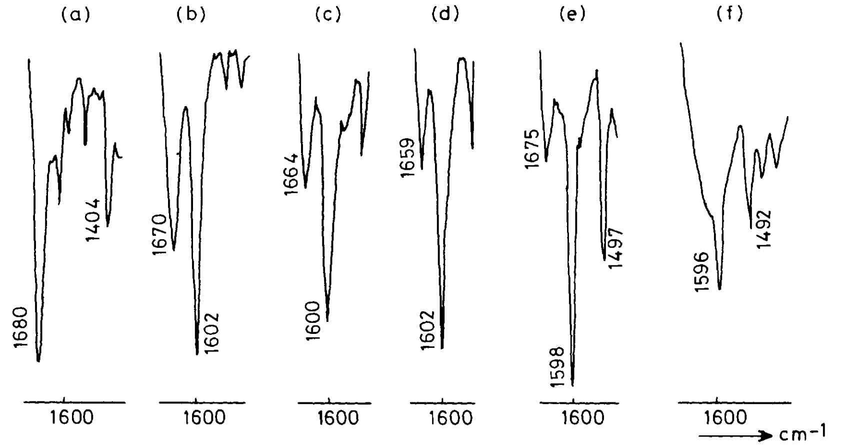

Figure 1. Part of the i.r. spectra of polymers (**3**): (a); (**7**): (b), (c), (d); and (**8**): (e), (f). The notations of the spectra refer to the notations in Table 1.

became electrically conducting with specific conductivities up to 0.1 S/cm (data are included in Table 1). The data found for polymer (**8**) were compared with data of the same polymer made earlier by the cross-Grignard coupling of 1,4-dibromobenzene and 2,5-dibromothiophene.[8] A large difference in conductivity is observed.

It had been shown earlier that 1,4-arylbutane-1′,4′-diones could be alkylated with a variety of substituents and that these products in turn were transformed into heterocycles.[9] Therefore, it is expected that the scope of this new synthetic route to polyaromatic polymers will not be limited to the examples described in this paper.

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