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NOVEL SYNTHESIS OF HETEROAROMATIC CONTAINING ELECTROACTIVE POLYAROMATICS OF KNOWN LINKAGES, ORDER, TOPICITY AND STOICHIOMETRY

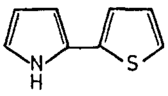
Andrew Pelter, Martin Rowlands and Ieuan H. Jenkins

Department of Chemistry, University College of Swansea,
Singleton Park, Swansea SA2 8PP, U.K.

Abstract: A novel Pd(0) catalysed process for the synthesis of electroactive mixed benzenoid-heteroaromatic polymers is given. The polymers resulting have predictable modes of linkage between different units and the ordering of the units is also fixed. The process can be used for different heterocyclic moieties and for the production of polymers containing the same units, in the same proportions and with the same order but with different topicities.

Polyaromatics and polyheteroaromatics have enormous potential, not only as organic metals[1] but also for their remarkable electrochemical properties.[2] Thus polypyrrole has been involved in the investigation of redox reactions,[3] as a protector for semiconductor photoanodes,[4] for high density storage information[5] and as an ammonia sensor.[6] Polythiophene has been used for electro-optical switching devices[7] and in all-polymer battery cells.[8] Substituted polythiophenes are considered ideal candidates for microsensor development,[9] and poly-1,3-bis(2-thienyl)benzene is an electrochromic polymer.[10] Substituted polyheteroaromatics can be soluble and can be used to give conducting polymers.[11] Poly(3-methoxythiophene) can be used for the controlled release of the neurotransmitter, glutamate.[12]

This glimpse of the potential applications of polyheteroaromatics casts into high relief the many inadequacies associated with their preparation. The most widely used method is the electrochemical oxidation of the monomer unit.[2] This process, even in the case of the polymerisation of a single heteroaromatic unit such as pyrrole, suffers from the gross defect that the structure of the polymer is undirected and undefined. Thus, although polypyrrole consists mainly of α-α'-linked pyrrole units, recent X-ray photoemission studies[13] show that as many as one in three pyrrole rings is affected by structural disorder, part of which is attributed to non α-α'-linkages. The situation in which <u>two</u> linked and different aromatic units are electrochemically polymerised is considerably worse. Thus the polymer derived from 1[14] can only be expressed by 2, in which the <u>order</u> of the units is unknown, as well as the positions of linkage, the degree of branching and the extent of cross-linking. The same is true of polymer 3,[15] and in fact 2 and 3 represent an enormous set of structures.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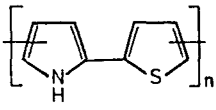
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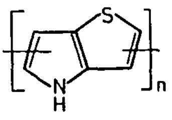
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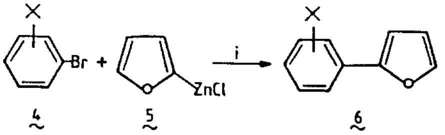
The main chemical syntheses of polyaromatics are equally unsatisfactory. Thus, oxidative polymerisation of pyrrole at a vapour-liquid interface gives a polypyrrole film with a structure no more defined than the electrochemical product.[16] The Friedel-Crafts polymerisation of benzene[17] to poly(p-phenylene) again gives no control of linkage position or the degree of branching or cross-linking.

Some very recent publications that detail the electrochemical oxidation of benzenoid-heteroaromatic oligomers prepared by nickel catalysed coupling processes,[10,18] together with a nickel catalysed production of thiophene oligomers,[19] prompt us to disclose our general approach to the synthesis of polyaromatics of carefully defined structure.

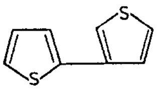
We recently reported the reaction shown in equation (1).[20]



(1)

$X = H$, 3- or 4-Me, 3- or 4-OMe, 3,4-di-OMe, 4-NO_2
i = cat $Pd(P\Phi_3)_4$, THF, Δ

The reaction proceeds smoothly with a variety of substituents on the benzene ring. Additionally, we have recently used it to couple a variety of thiophenes, so, for example, gaining ready access to 2,3'-bithienyl, 7. It is important to note that the positions of linkage of the products 6 are exactly defined by the structures of 4 and 5. We also reacted the bifunctional, 1,4-dibromobenzene (4, X = 4-Br) with monofunctional 5 to give 8, m.p. 148-150°C, λ_{max} 338 (4.02), (76%).



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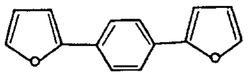

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We now report that 8 is readily converted to its bis-zinc chloride 9 (Fig.1), and that this bifunctional organometallic reacts with one equivalent of monofunctional 4, (R = H) to give 10,[21] m.p. 157-59°C, λ_{max} 352 nm (4.38), (58%) and with two equivalents of bromobenzene to give 11, m.p. 240-42°C, λ_{max} 373 nm (4.66), (87%). Compounds 8, 10 and 11 have had their structures confirmed by X-ray examination.[22] Reaction of bifunctional 9 with bifunctional, 1,4-dibromobenzene caused the formation and precipitation of polymer 12 (94%).

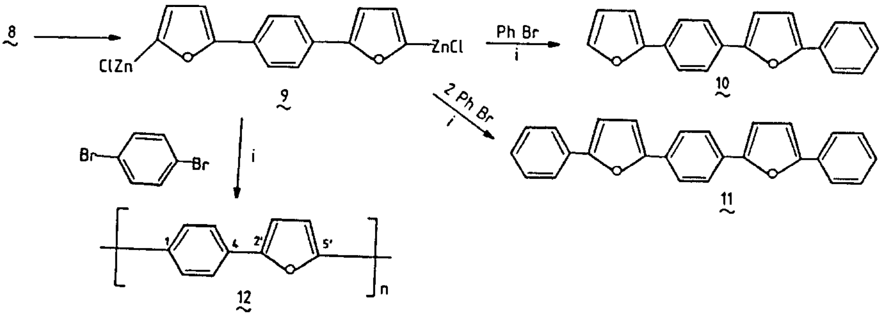
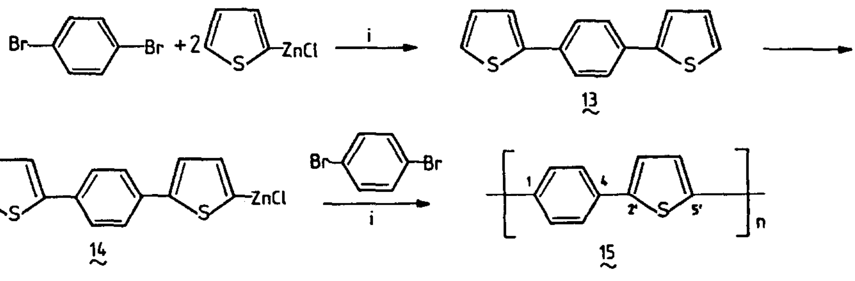


FIGURE 1

A similar set of reactions outlined in equation (2) yielded the bithienyl 13, m.p. 202-204°C, λ_{max} 320 nm (4.20) (72%),[23] and then the polymer 15 *via* the *bis*-zinc chloride 14.



(2)

Polymer 12 does not melt up to 360°C and shows no glass transition point. It is insoluble in all solvents tried and is recovered, apparently unchanged, from heating to red heat in air. Polymer 15 behaves similarly. Both polymers have been subjected to X-ray investigation.[22] They are highly crystalline with reflections observed to beyond 0.1 nm. Such high resolution is not normally associated with polymeric materials and emphasises the high chemical and structural regularity obtained using our new, transition metal catalysed polymerisation technique. The two polymers exist in an extended, approximately planar form with packing similar to poly(*p*-phenylene).[24] Polymers 12 and 15 are unique for the following reasons: (i) the units of which they are composed are unequivocally and solely linked 1,4- and 2'5' throughout; (ii) the order of the units is completely defined; (iii) the stoichimetry is defined; (iv) there is no branching nor cross-linking.

We have extended the process (Fig.2) to a polymer with same units as 12, joined in the same alternant order but with a different and defined topicity. Both polymers are part of the set expressed by 19. Thus, reaction of 1,3-dibromobenzene (4, X = 3-Br) with 5, yielded 16, m.p. 37-38°C, λ_{max} 280 nm (4.53) (70%). The *bis*-zinc chloride, 17, reacted with 1,3-dibromobenzene to yield polymer 18 in 85% yield. The conformation of this fascinating, potentially spiral polyaromatic is being studied.[22]

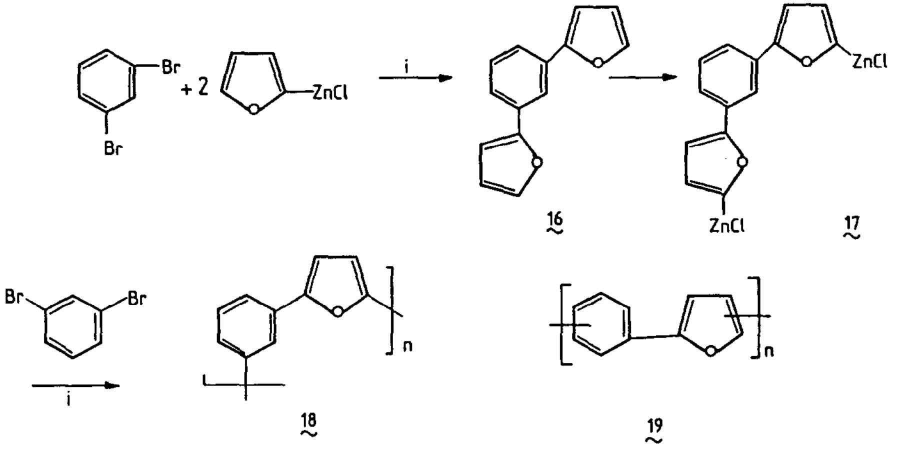


FIGURE 2

In summary we have shown that a novel Pd(0)-catalysed polymerisation process yields polyaromatics with highly desirable characteristics. Different heteroaromatics can be incorporated to give polymers of known order and with known linkage points. The shape of the molecules may be altered at will by choice of the correct dibromides (compare **12** and **18**). The process appears to be general, both in terms of the heteroaromatics and the dibromides used. The bromide need not be benzenoid, as shown by the production of **7** in 70% yield, from 2-thienylzinc chloride and 3-bromothiophene. The original reaction will tolerate both electron attracting and donating groups on the benzene ring, thus opening the way to the production of alkylated polymers and polymers with regularly placed, charged groups. Clearly the reaction described is capable of yielding a plethora of electroactive polymers, and its scope and limitations are being explored.

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