Russian Chemical Reviews **65** (9) 785–795 (1996)
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UDC 541.64

Polycondensation reactions catalysed by Ni and Pd complexes as the method for the synthesis of carbo- and hetero-cyclic polyarylenes

A L Rusanov, I A Khotina

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Abstract. Data on the application of the method of polycondensation cross-coupling catalysed by Pd and Ni complexes for the synthesis of carbo- and hetero-cyclic polyarylenes are systematised and generalised. The bibliography includes 126 references.

I. Introduction

Until recently, the chemistry of carbo- and hetero-cyclic polyarylenes has been among the less studied fields of science on high-molecular compounds.[1] Despite the numerous attempts of investigators to develop new approaches to the synthesis of carbocyclic[2–11] and heterocyclic[12,13] polyarylenes, the synthesis of high-molecular polymers having a clearly defined structure seemed to be highly problematic.

The methods of polyarylene synthesis are classified as direct and indirect ones. Direct syntheses employ the monomers already containing the aromatic units, which then become repeating units of the polymers. Characteristic examples of direct polyarylene synthesis are the synthesis of poly-*p*-phenylene according to Kovacic[9] or using electrochemical methods.[14,15]

In the case of indirect syntheses, a prepolymer is first prepared, which is converted into polyarylene under the action of definite factors (e.g., thermal treatment). This can be exemplified by the synthesis of insoluble poly-*p*-phenylene starting from a soluble prepolymer, a derivative of poly(5,6-dihydroxy-cyclohex-2-en-1,4-ylene); its pyrolysis gives insoluble poly-*p*-phenylene.[8,12] The transformation of high-molecular, stereoregular poly(5,6-dicarboxycyclohex-2-en-1,4-ylene) into poly-*p*-phenylene in the presence of H_3PO_4 at 100–250 °C has been described.[16]

Unfortunately, both the direct and indirect methods have serious disadvantages. The conditions required for the direct polyarylene synthesis are too drastic for the regiospecific reactions. Therefore, in the case of polyphenylene not only 1,2-, 1,3- and 1,4-disubstituted phenylene fragments of the chain but also trisubstituted units can be formed. Moreover, the molecular weight of the polyarylenes obtained by direct methods are usually low due to the insolubility of polyarylenes.

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Received 13 July 1995
Uspekhi Khimii **65** (9) 852–864 (1996); translated by R L Birnova

The indirect method can be used to obtain polyarylenes with high molecular weight; however, the units in the polymers thus formed are not uniform[17] due to the incompleteness of the prepolymer conversions.

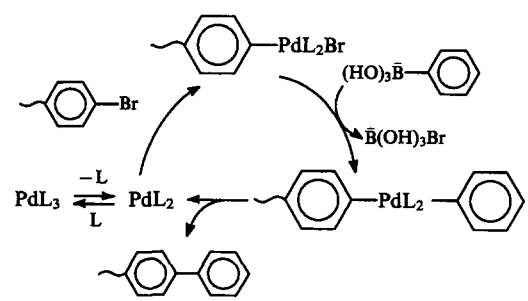
The analysis of literature data revealed that the development of direct methods that would not require drastic conditions for their realisation is the most promising approach to progress in polyarylene chemistry. The problem of polymer solubility must be solved in parallel. The most suitable to this end are polycondensation reactions based on haloaromatic compounds catalysed by transition metal complexes.

II. Synthesis of polyarylenes by cross-coupling catalysed by palladium complexes

1. Synthesis of carbo- and hetero-cyclic polyarylenes by interaction of arene dihalides with aromatic diboronic acids or their derivatives

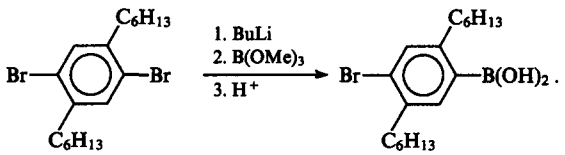
The first application of cross-coupling reactions catalysed by palladium complexes to the synthesis of polyarylenes was described by Suzuki[18] and Muller.[19] These authors demonstrated that different monobromoaromatic compounds react with benzeneboronic acid or its cyclic esters to give high (up to 99%) yields of products.

The same reactions have been described in more recent works.[20–22] The following scheme for this process has been proposed by Suzuki:[23]

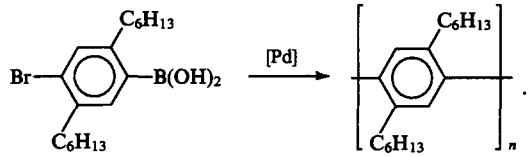


Later, cross-coupling reactions were used for the synthesis of polyarylenes. A great advantage of the polycondensation cross-coupling method is the possibility of introducing various side groups (aliphatic, aromatic, ester, etc.) into the monomers. On the one hand, by introducing side groups one may improve the solubility of the polymers (which is important for their processing) and, to some extent, increase their molecular weight. On the other hand, the use of these groups may confer specific (liquid crystalline, conducting, nonlinear optical) properties on the

polymer. Cross-coupling reactions have been used, in particular, in the synthesis of alkyl-substituted poly-*p*-phenylenes. The starting monomers were obtained by the treatment of 2,5-dialkyl-1,4-dibromobenzenes with 1 equiv. of *n*-butyllithium followed by addition of trimethylborate and acid hydrolysis:[24]



Homopolycondensation of this monomer in the presence of $Pd(Ph_3P)_4$ in benzene and subsequent addition of concentrated Na_2CO_3 solution give a colourless polymer soluble in organic solvents:[24]



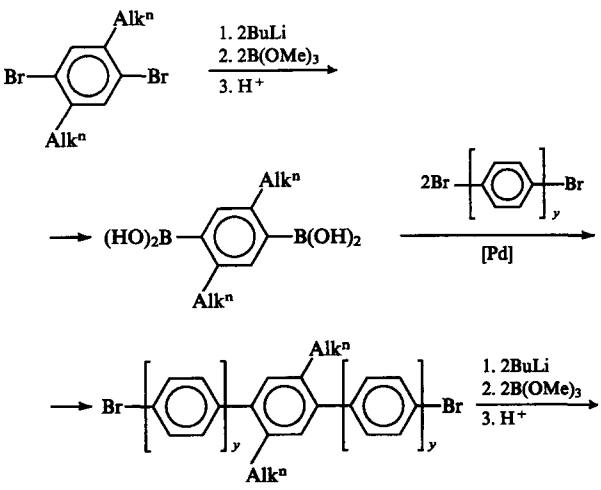
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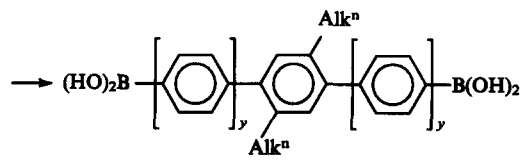
The degree of polymerisation (DP) of the polymer **1** reached 30. The analysis of ^1H and ^{13}C NMR spectra revealed that this reaction is highly regiospecific. The yield of the polymer in this reaction was 100%.

It is noteworthy that in the majority of polycondensation cross-coupling reactions the yields of the polymers vary from 80% to 100% depending on the solubility of the synthetic polymer and its molecular weight.

Clearly, if bulky alkyl groups were not introduced into the original monomers, no poly-*p*-phenylenes with DP 30 could be obtained. However, the introduction of these groups plays not only a positive role. In some instances, the introduction of bulky substituents results in conformational changes in the polymer chain, e.g., in disturbance of the coplanarity of the adjacent phenyl groups.[25-28] Minor departures from coplanarity have no appreciable influence on the electrical and optical characteristics of the polymers; however, if these deviations exceed a certain level, the properties of the polymers change drastically.[29]

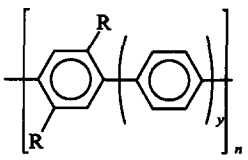
Similar approaches were used to obtain polyphenylenes,[24] in which the blocks of unsubstituted *p*-phenylene fragments of varying length were connected via phenylene cycles containing side alkyl groups.[30] The synthesis of the original monomers was carried out in accordance with the following scheme:





$y = 1-6$.

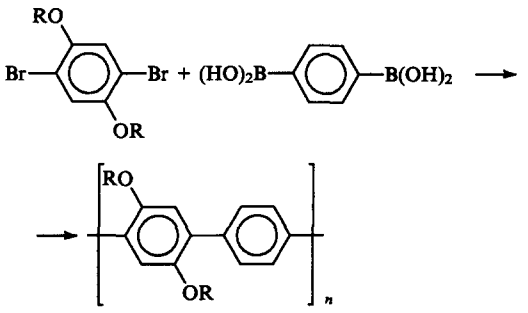
Thus, by combining various diboronic acids with dibromo compounds one can obtain polymers with the general formula:[30]



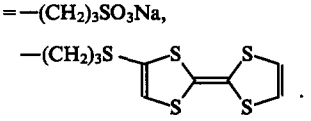
In some cases ($y = 2$), the target products with the molecular weight M_n of 21 000 were synthesised, which corresponds to a degree of polymerisation of 37. In this case, the total number of phenylene groups may amount to 100. To date, this polymer has the highest degree of polymerisation among those obtained by Pd-catalysed polycondensation cross-coupling.

The synthesis of polymers with side alkoxy groups based on dibromides and diboronic acids has been described.[1] A significant advantage of the polycondensation cross-coupling method is the high activity of diboronic acids and their insensitivity with respect to water (e.g., in some of these reactions, an aqueous solution of Na_2CO_3 was used). In some instances, water-soluble palladium complexes, sodium tris[(trisulfonatophenyl)phosphine]palladium(0) (**2**) and sodium (or potassium) tris[(diphenyl-*m*-sulfonatophenyl)phosphine] palladium(0) (**3**), were used as catalysts.[31,32]

The synthesis of water-soluble polymers containing sulfonatoalkoxy groups has been described:[33,34]

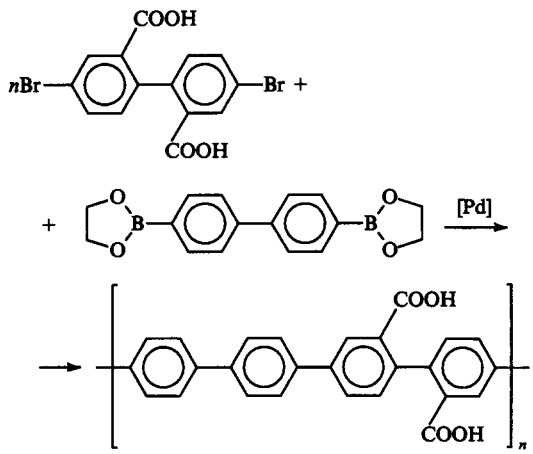


R = $-(CH_2)_3SO_3Na$,



The reactions were carried out in an aqueous medium, to which DMF and K_2CO_3 were added. Palladium complexes **2** or **3** were used as catalysts. The molecular weight was not determined, but, as could be judged from the low bromine content in the polymer based on sodium of 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene and benzene-1,4-diboronic acid (0.5%), it was of about 15 000.

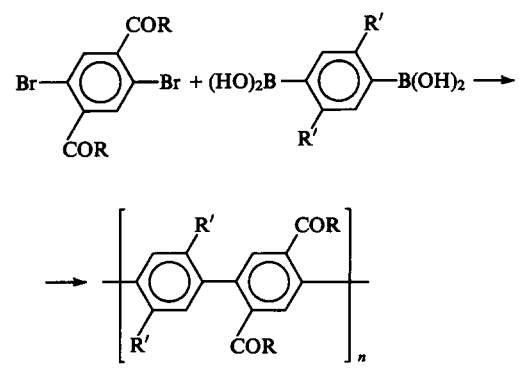
Other water-soluble poly-*p*-phenylenes[23,32] carrying carboxyl and carboxymethyl groups have also been described. Thus, the polymer **4** with a molecular weight of about 10 000 (DP ~ 25) was synthesised based on 4,4′-dibromo-2,2′-dicarboxybiphenyl and a cyclic ester of 4,4′-biphenyldiboronic acid. The polycondensation reaction was carried out in a weakly alkaline solution (H_2O–DMF, 3 : 1) in the presence of a water-soluble Pd-catalyst.[31]



4

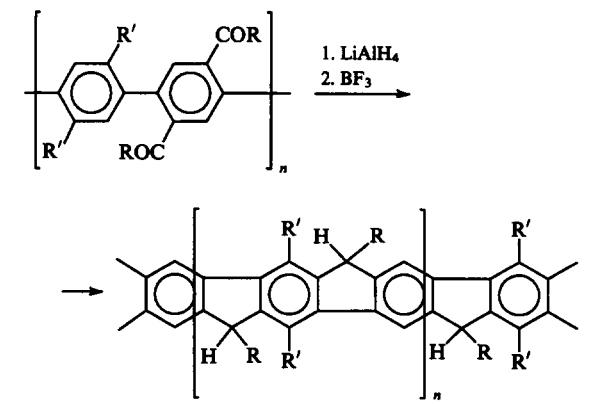
It is noteworthy that cyclic diboronates are more preferable than diboronic acids because of their better solubility and ease of purification.

Also, polycondensation was successfully employed in the synthesis of prepolymers of ladder systems.[35-38] Mullen et al.[35,38] performed the synthesis of soluble prepolymers based on dialkyl-substituted benzenediboronic acids and dibromobenzenes containing keto, aldehydo, and other groups:



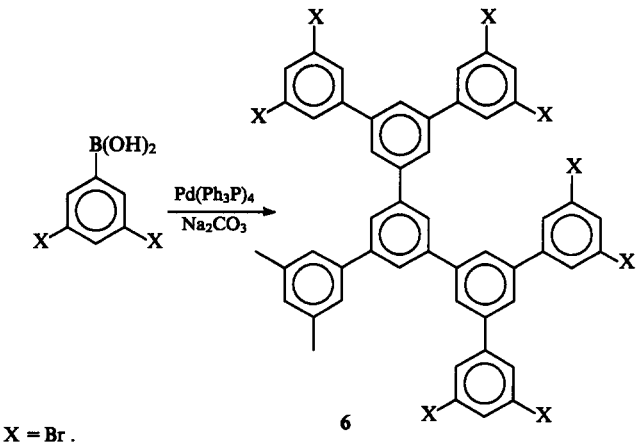
R = H, $C_{10}H_{21}$; R′ = C_6H_{13}.

Subsequent intramolecular cyclisation converted them into ladder structures devoid of non-cyclised fragments.



The ladder polymers **5** have been synthesised from the prepolymer ($\bar{M}_n$ = 7800) based on substituted dibromobenzene carrying acetylene groups and cyclic benzenediboronate (Scheme 1).[39]

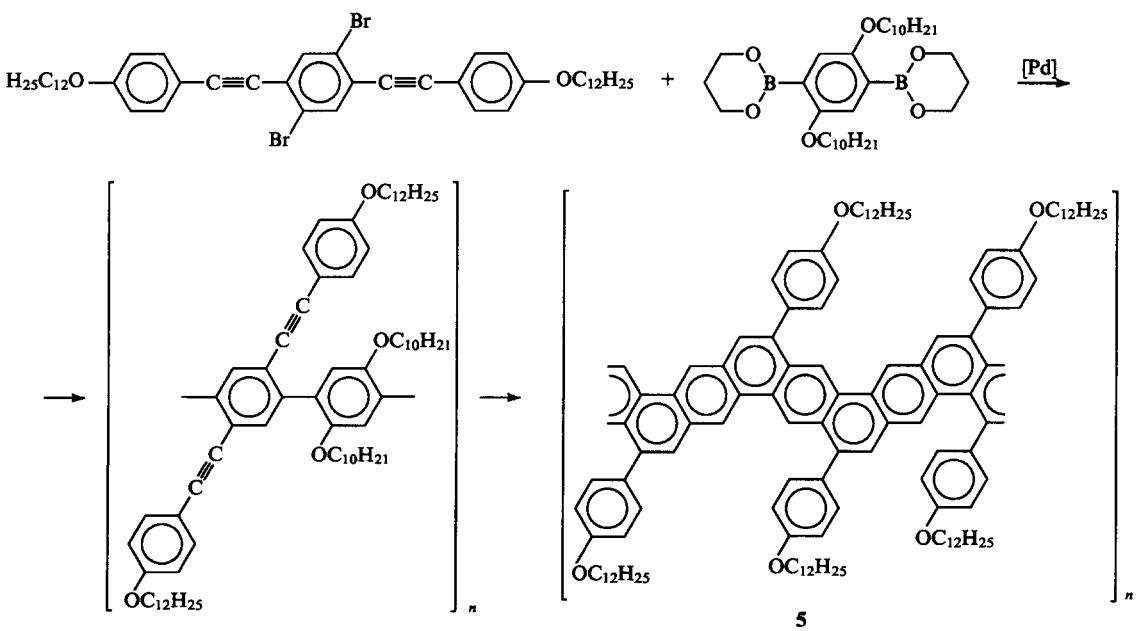
Besides difunctional monomers or monomers of the AB-type, the Pd-catalysed cross-coupling reactions also involve trifunctional benzene compounds of the ABB type. The latter were used to obtain the polymeric dendrites (**6**):[40,41]



X = Br.

The yield of the product was 80%–95%, $\bar{M}_n$ = 3820 and $\bar{M}_w$ = 5750. It was readily soluble in THF and *o*-dichlorobenzene.

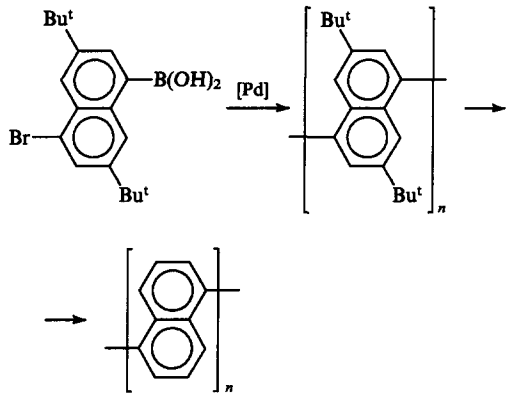
Scheme 1



5

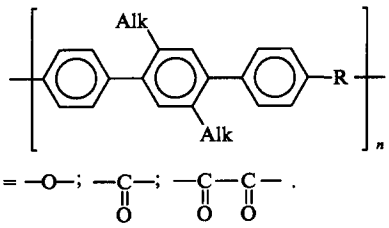
Its viscosity (0.031 dl g^{-1} in THF) was very low which is characteristic of highly branched oligomers. The oligomer **6** had a T_g = 280 °C and did not melt.

Polycondensation cross-coupling is also used in the synthesis of naphthalene compounds. Using this route, a soluble poly(1,5-naphthalene) with a low degree of polymerisation has been synthesised:[42,43]



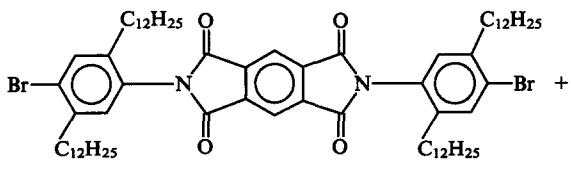
To obtain thermostable polymers, the *tert*-butyl groups are removed from the polymer in alkaline media or by thermal treatment. In this context, the *tert*-butyl groups have a clear advantage over linear alkyl substituents.

A great number of investigations in the area of polycondensation cross-coupling were concerned with the synthesis of polyarylenes and related aromatic polymers containing —O— and —CO— groups in their main chains. Thus, the interaction of the 4,4′-dibromodiphenyl ether, 4,4′-dibromobenzophenone or 4,4′-dibromobenzyl with dialkyl-*p*-phenylenediboronic acid gave the corresponding alkyl-containing aromatic polyether, polyketone, and poly-α-diketone.

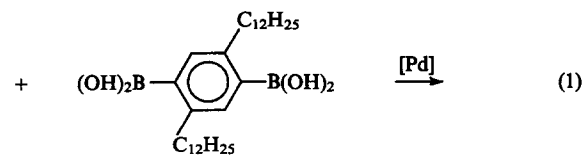


The presence in the side chains of alkyl substituents renders these polymers soluble in ordinary organic solvents.

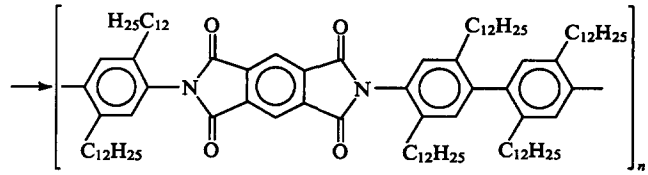
The cross-coupling reaction opens up new opportunities for the synthesis of such polymers as substituted polyimides.[44–46] Recently,[44] defect-free polyimides **8** based on didodecylphenyldiboronic acid and the dibromide **7** containing imide rings have been synthesised in a heterogenous medium (aqueous solution of Na_2CO_3/toluene) in the presence of the Pd^0 catalyst, $Pd(Ph_3P)_4$.



7



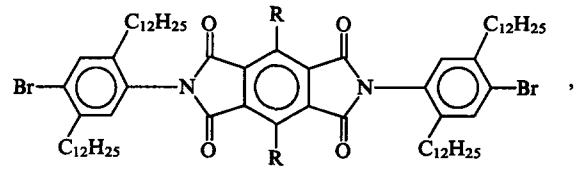
(1)



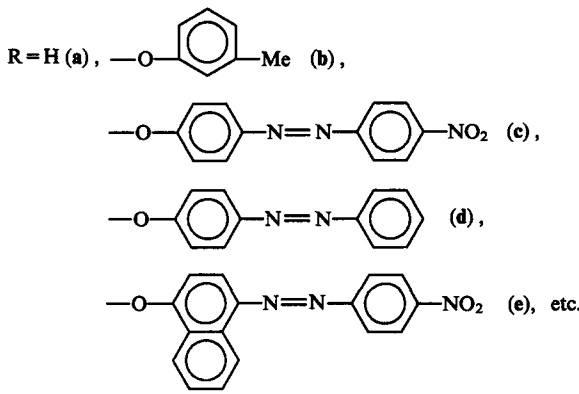
8

The molecular weight of the polymer **8**, $\bar{M}_n$, equalled 20 000, which corresponded to a DP of 14. Such polymers can be obtained by conventional polycondensation of dianhydrides and diamines;[47] however, in some cases (see, for example, Ref. 46) direct synthesis of the polymers seems to be problematic.

Other imide-containing dibromides, such as the compounds cited in Ref. 46 can also be introduced into the reaction (1):



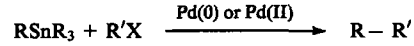
9



Here, the radicals R are the residues of dyes which are nonlinear, optically active chromophores. The dibromides **9b–e** enter into the polycondensation reaction with difficulty due to steric hindrances. In this case, up to 50% of the dibromide 9a was introduced into the reaction simultaneously with the dibromides **9b–e**. The molecular weights of the copolymers so obtained were not very high, they amounted to 17 000 (50% **9a** + 50% **9b** copolymers), whereas the molecular weight of the polymer obtained from dibromide **9a** alone was 41 000 (DP = 11 and 26, respectively).[46]

2. Synthesis of polyarylenes with participation of aromatic organometallic compounds

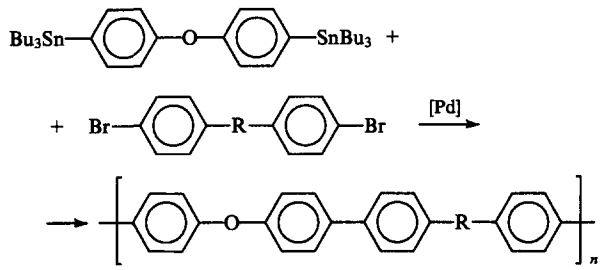
Considerable attention has been recently given to Pd-catalysed reactions between aromatic dihalides and bis(trialkylstannyl) compounds. The chemical stability and ease of purification of organotin compounds have motivated their wide-scale application in organic chemistry.[48–51]



R, R′ = aryl, alkyl, alkenyl and alkynyl.

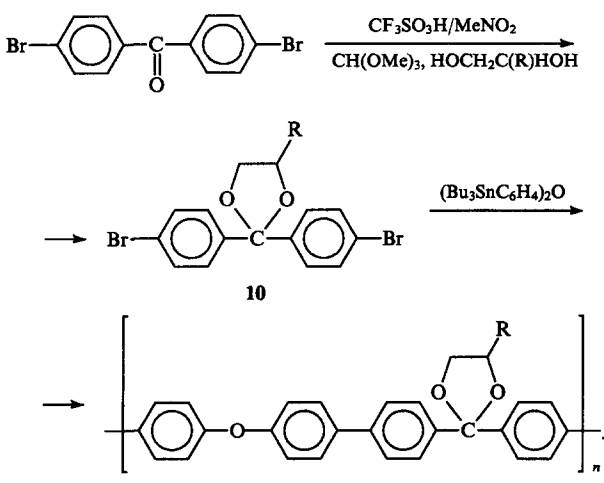
This reaction was first described for aromatic tin derivatives and aromatic halides in Ref. 51. The interaction of bisstannyl compounds and aromatic dihalides was employed in the synthesis of polyarylenes. Thus, the interaction of 4,4′-bis(tributylstannyl)diphenyl ether with various aromatic dihalides[52,53] [e.g., with 4,4′-dibromodiphenyl ether (**a**), 4,4′-dibromobenzophenone (**b**), and 4,4′-dibromodiphenyl sulphone (**c**)], in the presence of

$PdCl_2(Ph_3P)_2$ in dipolar aprotic solvents gives the polymers whose molecular weights [as can be judged from their residual bromine content 5.2 (**a**), 1.69 (**b**), and 0.9% (**c**)] are 1500, 4800, and 8000, respectively. All the synthetic polymers are poorly soluble in organic solvents; their molecular weights increase with an increase in the polymer solubility. It has been possible to measure the inherent viscosity for the latter polymer, which was equal to 0.22 dl g^{-1}.



R = −O−(**a**), −C(O)−(**b**), $-SO_2-$(**c**).

4,4′-Bis(tributylstannyl)diphenyl ether was also used in the synthesis of soluble polyarylenes based on 4,4′-dibromobenzophenone.[54] Insoluble 4,4′-dibromobenzophenone was converted into the soluble acetal. The reaction was carried out according to the following scheme:

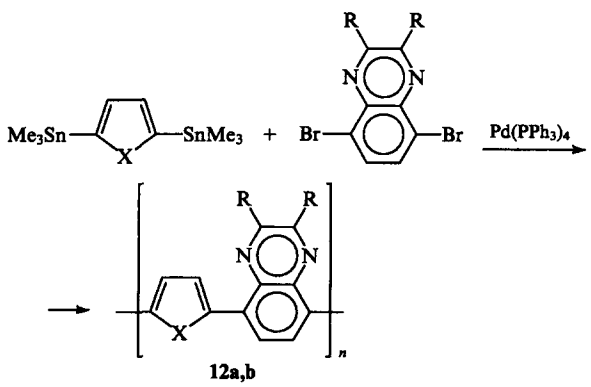


10

11

After polycondensation, the acetal groups can be transformed into the ketone groups. The molecular weight of the polymer **11** obtained from the acetal **10** exceeds 25 000 (DP > 74).

Recently, the synthesis of polymers with alternating electron-deficient substituted quinoxaline cycles and electron-donor thiophene or furan groups, has been carried out.[55]

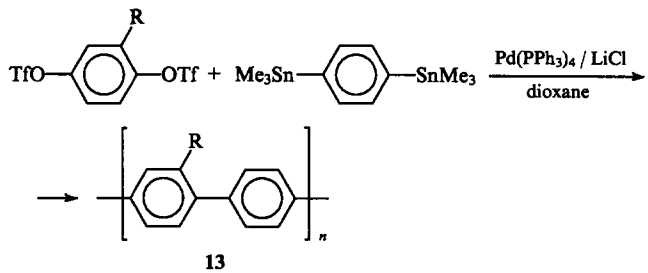


12a,b

R = C_7H_{15}, Ph; X = S (**a**); O (**b**).

The yield of the polymers was 96% and the reduced viscosities varied from 0.37 to 0.47 dl g^{-1}. The polymers **12a,b** represent structures with charge transfer between the electron-donor and electron-acceptor groups, which eventually determines their intriguing physical properties.

Another synthetic procedure that makes use of the Pd-catalysts involves the interaction of bistrifluoromethanesulfonates (bistriflates) with bisstannin compounds (in some cases, with aromatic dihalides). Triflates are readily formed from the accessible hydroquinones by their interaction with triflic (trifluoromethanesulfonic) anhydride, $(CF_3SO_2)_2O$ (Tf_2O). This approach applied to alkyl-containing bistriflate and bis(trimethylstannyl)benzene with catalysis by $Pd(Ph_3P)_4$ and LiCl resulted in alkyl-containing polyphenylenes **13**.[56,57]



13

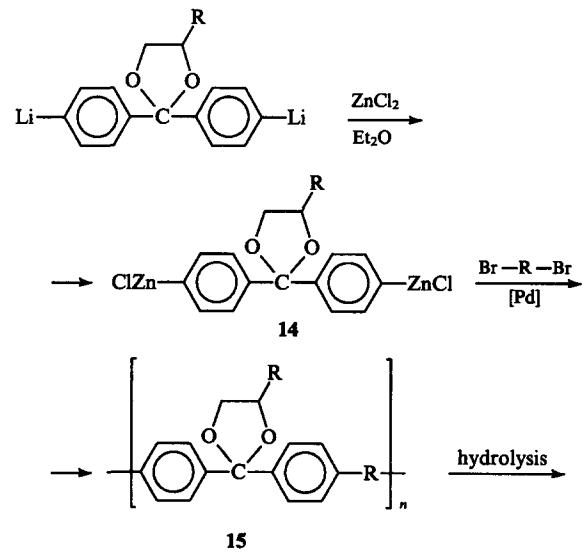
Tf = CF_3CO_2;

R = $(CH_2)_{10}COOC_2H_5$, $(CH_2)_xCH_3$ (x = 5, 7, 11).

The maximum molecular weight of the resulting oligomer, $\bar{M}_n$, was 6400.

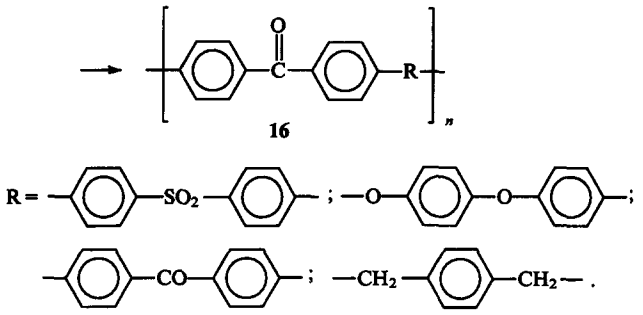
The palladium-catalysed cross-coupling also makes use of the reactions with other organometallic compounds.[58] Thus, polycondensation of aromatic dihalides with organotin compounds as well as their interactions with Grignard (see below) and Zn-reagents have been described.[53] One of Zn-reagents was synthesised from the corresponding diphenyl ether by transmetallation. Its interaction with 4,4′-dibromodiphenyl ether, 4,4′-dibromo-*p*-xylene, and 4,4′-di(bromomethyl)benzene in the presence of $PdCl_2(Ph_3P)_2$ in THF was used to synthesise the corresponding oligomers. Of them, the oligomer based on 4,4′-di(bromomethyl)benzene had the highest molecular weight (3100).

Polycondensation of the Zn-reagent **14** obtained from the acetal of 4,4′-dilithiobenzophenone with dibromoderivatives of some aromatic compounds has been carried out.[54]



14

15



16

The maximum molecular weight of the acetal polymer **15c**, $R=(C_6H_4)_2SO_2$, is not high being up to 6730 (DP = 19).

The crystalline polymer **16** obtained by hydrolysis of the prepolymer **15** has $T_g=208$ °C and m.p. 380 °C. As regards its crystallinity and other properties, the polymer **16** is closely related to polybiphenylene ether sulfones obtained by other methods.

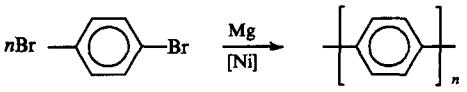
In general, the molecular weights of the polymers based on Zn-reagents are lower than those based on Sn-compounds, apparently due to the better solubility of the latter.

Thus, the use of the polycondensation cross-coupling method in the presence of Pd^0 and Pd^{II} complexes makes it possible to obtain polymers whose molecular weights do not exceed 20000–25000. These reactions can be carried out in aqueous media.

III. Synthesis of polyarylenes by cross-coupling catalysed by nickel complexes

1. Synthesis of polyphenylenes and polyarylenes using Grignard reagents

The cross-coupling reaction of dihalogenoaromatic compounds with Grignard reagents in the presence of various catalysts including predominantly bivalent Ni was first described by Yamamoto[59, 60] in 1977–78. Thus, the interaction of 1,4-dibromobenzene with 1 equiv. of Mg and a catalytic amount of $NiCl_2$(bipy) (bipy = 2,2′-bipyridyl) or other Ni^{II} compounds in boiling THF resulted in a polymer, which contained exclusively *p*-phenylene groups, with DP of up to 24.



This polycondensation reaction was based on the synthesis described by Tomao and Kumada in 1972.[61]

$$RMgX + R'X \xrightarrow{NiX_2L_2} R-R' + MgX_2.$$

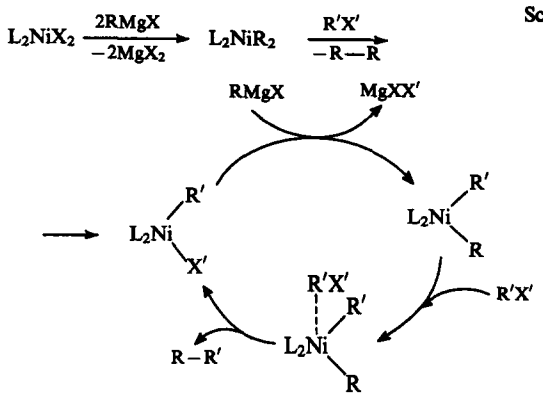
This reaction proceeds selectively and quantitatively under mild conditions.

Later, studies of cross-coupling of aromatic halides and Grignard reagents were further continued in the works,[22, 62–65] in which not only Ni^{II} but, for the most part, Ni^0 complexes have been used as catalysts. The most probable mechanism for this reaction can be schematised as depicted in Scheme 2.[63]

An attempt has been made[57] to obtain polymers from 4,4′-dibromodiphenyl ether and the Grignard reagent prepared from it. Polycondensation was performed in the presence of $NiCl_2$(dppp) [dppp = 1,3-bis(diphenylphosphino) propane]. However, the final products appeared to be insoluble in the majority of organic solvents and had a low molecular weight (up to 600).

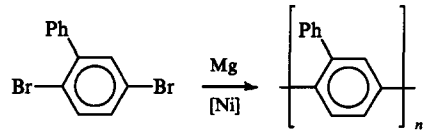
Two most likely reasons for the termination of growth of the poly-*p*-phenylene chain are: (i) the decrease of the product solubility in the course of polycondensation and its precipitation; (ii) chemical factors preventing the growth of the macromolecular chain, such as hydrolysis of its active end.

Scheme 2



The fact that phenylene and, particularly, flexible side alkyl groups improve the solubility of low-molecular compounds[66–69] and polymers[70–72] predetermined future lines for development of investigations in the field of synthesis of polyphenylenes and polyarylenes based on Grignard reagents, viz., the use of monomers carrying side groups.

Poly(phenyl-1,4-phenylene)[73] was synthesised by using the Yamamoto reaction.[59] 2,5-Dibromobiphenyl was treated with an equimolar amount of Mg in THF and then 1.13 mol % of a nickel catalyst, $NiCl_2(Ph_3P)_2$, was added:



The final product was soluble in chloroform; its molecular mass, $\bar{M}_w$, was 1100–2200 (in some cases, the proportion of an insoluble fraction constituted 13%).

The use of 1,4-dibromobenzene containing side alkyl groups [R = Alk (C_6–C_{12})] as monomer resulted in the polymer $[-C_6H_2R_2-]_n$.[74]

The synthesis of n-alkyl-substituted poly-*p*-phenylenes was carried out under conditions described above. The reaction mixture was homogeneous; however, in this case, too, the degree of polymerisation did not exceed 13. The following Ni^{II} compounds were used as catalysts: Ni(bipy)Cl_2, Ni$(Ph_3P)_2Cl_2$, Ni(acac)$_2$, and Ni(dppp)Cl_2 (acac is acetylacetonate). Among those, Ni$(Ph_3P)_2Cl_2$ turned out to be the best catalyst, for it gave the polymer of the highest molecular weight.

Conducting polyarylenes, polytriphenylamines[75] soluble in benzene and chloroform were synthesised based on 4,4′-dichlorotriphenylamine (**a**) and 4,4′-dibromo-(4″-methyl)triphenylamine (**b**) by Ni-catalysed polycondensation using Grignard reagents. Ni(bipy)Cl_2 was used as the catalyst; it was added only after the formation of the Grignard reagent. This procedure made use of metallic Mg obtained *in situ* by reduction of anhydrous $MgCl_2$ with metallic potassium. The yield of the oligomers was 63% and 71%, respectively; the degree of polymerisation did not exceed 12.

From the above examples it can be seen that if the polycondensation is performed with the Grignard reagents, the solubility is not crucial in the preparation of high-molecular-weight polymers. The most probable reason for the termination of the chain growth in these reactions is purely chemical, i.e., hydrolysis of Mg-containing terminal fragments by trace amounts of moisture. Moreover, all the polycondensation reactions based on the use of Grignard reagents were carried out in THF, which could also restrict the growth of the polymeric chain.

Hence, the application of Grignard reagents in the cross-coupling reaction is limited due to the fact that they can give rise only to oligomeric products.

2. Synthesis of polymers using Ni^0 complexes

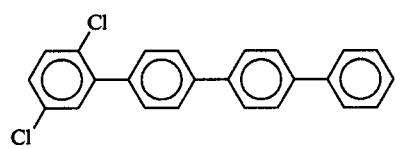
a. Homocondensation of dihaloaromatic compounds

For the first time, the condensation of aryl bromides or iodides in the presence of Ni^0 complexes in dipolar aprotic solvents has been described in Refs 76–78.

These reactions proceeded under mild conditions but had a number of limitations: (i) their realisation required large amounts of the catalyst, the catalyst to monomer ratio being 1 : 1; (ii) the reaction conditions must be such that traces of air and moisture must be avoided.

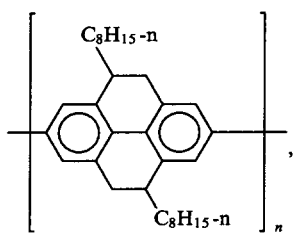
Using this method, Yamamoto et al.[79,80] succeeded in obtaining poly-*p*-phenylenes and other polyarylenes. As a catalyst, $Ni(COD)_2$ (COD = cycloocta-1,5-diene) was used. Neutral ligands (Ph_3P or bipy) were also added to the reaction medium. Thus, oligomers with molecular weights of up to 6000 were synthesised based on *p*-dihalobenzenes.[79] The use of 9,10-dibromoanthracene as monomer gave a stable complex, $L_mNiX(C_6H_4X)$, in high yield; in this case, the oligomer was not formed. Hence, it follows that chain growth also depends on the monomer structure.

Poly-*p*-phenylenes carrying pendant *ter*-phenyl groups have been synthesised[81] from 2,5-dichloroquaterphenyl



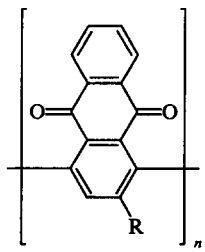
in the presence of the same catalyst, [$Ni(COD)_2$ + bipy)] in DMF; they possess intriguing properties (as regards their conductivity); however, the degree of polymerisation did not exceed 10.

In more recent syntheses employing this catalyst, polymers of higher molecular weights could be obtained, apparently due to perfection of the synthetic procedure, i.e., more extensive purification of monomers and better removal of traces of moisture and oxygen from the reaction medium. Thus, Mullen et al.[82] succeeded in obtaining soluble poly-*p*-phenylene:



based on the dibromide of substituted tetrahydropyrene; its molecular weight was 35 000 ($\bar{M}_w$) or 17 400 ($\bar{M}_n$) (DP = 40).

Later, Yamamoto[83] synthesised polyanthraquinone and polymethylanthraquinone of high molecular weights (~190 000) from dichlorides:



R = H, Me.

An alternative pathway was also proposed.[84–86] A reactive Ni^0 catalyst was prepared from catalytic amounts of $NiCl_2(Ph_3P)_2$ (or $NiCl_2$) in the presence of excess Ph_3P and a large excess of Zn powder (or some other reducing metal) at 60–80 °C in dipolar aprotic solvents. The reaction was completed within several minutes.

The positive factor in the use of these Ni^0 catalysts is that aryl chlorides are most active in this process, as distinct from processes described earlier, in which aryl bromides and aryl iodides possess the highest activity.

The putative mechanism of this reaction can be illustrated by the following scheme with the synthesis of a bisarene as an example:[84]

$$Ni^0L_3 + ArCl \xrightarrow[-L]{} ArNi^{II}ClL_2 \quad (1)$$

$$ArNi^{II}ClL_2 + \tfrac{1}{2}Zn \xrightarrow{L} ArNi^{I}L_3 + \tfrac{1}{2}ZnCl_2 \quad (2)$$

$$ArNi^{I}L_3 + ArCl \xrightarrow[-L]{} Ar_2Ni^{III}ClL_2 \quad (3)$$

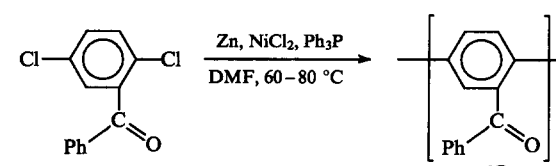
$$Ar_2Ni^{III}ClL_2 \xrightarrow{L} Ar-Ar + Ni^{I}ClL_3 \quad (4)$$

$$Ni^{I}ClL_3 + \tfrac{1}{2}Zn \longrightarrow Ni^0L_3 + \tfrac{1}{2}ZnCl_2 \quad (5)$$

L = PPh_3.

It has been shown that the first step (oxidative attachment of ArCl to Ni^0 to form a bivalent nickel complex) occurs at rather a high rate. The next step, i.e., the reduction of Ni^{II} to Ni^{I}, is slow and rate-limiting at the beginning of the reaction when the ArCl concentration is still high. At the end of the reaction, it is the third step that determines the reaction rate. It has been found that the second and third rate-limiting steps are accelerated by the introduction of electron-acceptor substituents into the benzene rings and, *vice versa*, are decelerated with the introduction of electron-donor substituents. In addition, in the presence of electron-donor substituents side reactions can take place, viz., the formation of ArH. This is due to the fact that electron-donor groups stabilise the coordinatively unsaturated Ni^{I} complex, and the transfer of the phenyl group from the phosphorus to the nickel atom is possible. As the reaction proceeds further, this reaction course can result in the termination of the polymer chain and, consequently, in the synthesis of a low-molecular weight polymer.

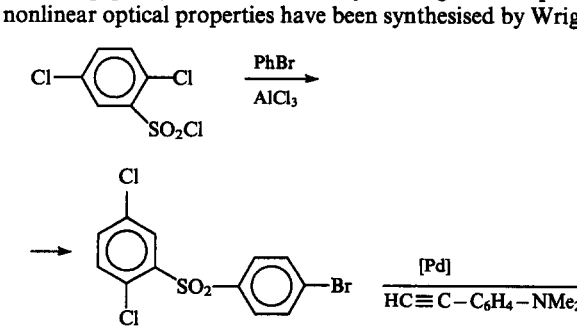
This method was used to obtain soluble poly-*p*-phenylene **17** based on 2,5-dichlorobenzophenone.[87,88]

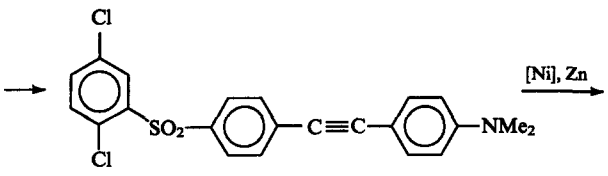


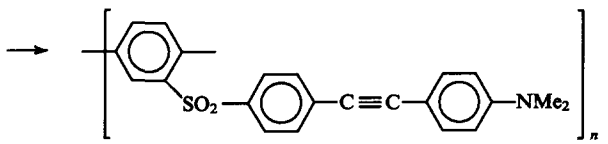
17

The polymer **17** possessed a high inherent viscosity: 1.05 dl g^{-1} when the reaction was carried out for 7 h, and 1.3 dl g^{-1} when the reaction was carried out run for 50 h ($\bar{M}_w$ = 60000, DP = 330, T_g > 205 °C). The polymer was soluble in $CHCl_3$, in $PhOH-CH_2Cl_2$ and $PhOH-C_2Cl_4$ mixtures, formed films, and retained stability in air at temperatures below 500 °C (TGA).

Poly-*p*-phenylenes with side acetylene fragments **18** possessing nonlinear optical properties have been synthesised by Wright.[89]







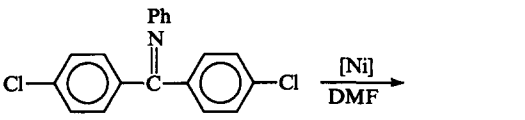
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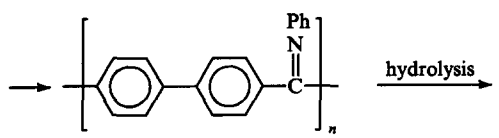
The polymer **18** had a low molecular weight ($\bar{M}_n$ = 8000) and was readily soluble in ordinary organic solvents. Its glass transition temperature, T_g, is 220 °C, and its thermal stability is 300 °C (according to TGA).

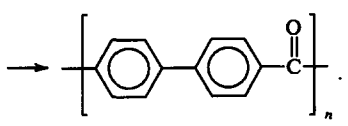
The synthesis of polyether sulfones $[-C_6H_4-SO_2-C_6H_4-O-C_6H_4-C_6H_4-O-]_n$ and polyether ketones with the following formulae: $[-C_6H_4-C(O)-C_6H_4-X-C_6H_4-C(O)-C_6H_4-]_n$ where X = O, OC_6H_4O, has been described.[90-92] 4,4′-Bis(*p*-chlorophenyloxy)diphenylsulfone was used as the main monomer during the synthesis of polyether sulfones. Copolymers of 4,4′-bis(*p*-chlorophenyloxy)diphenylsulfone with 4,4′-dichlorodiphenyl sulfone, *p*-dichlorobenzene, etc, were also obtained. Of all polymers, the homopolymer possessed the largest reduced viscosity (0.81 dl g^{-1}); the viscosities of copolymers (in *N*-methylpyrrolidone at 25 °C) were in the range 0.4–0.69 dl g^{-1}.

The efficiency of homopolycondensation and, correspondingly, the molecular weight of the polymers obtained in the presence of Ni^0 complexes depends on three factors. The most important is the absence of moisture, since in the presence of water aryl halide is reduced to arene,[93] eventually resulting in the termination of the chain. The second factor is the inert atmosphere, since even very small amounts of oxygen deactivate the catalyst (nickel oxide formed upon oxidation is not a catalyst under these conditions). The third factor is the purity of Zn (this must possess a well-developed surface and be free of oxygen).

The synthesis of polyarylenes involving Ni^0 catalysts has also been described in many other papers. Thus, 1,2-bis(4-chlorophenyl)- and 1,2-bis(3-chlorophenyl)-1,1,2,2-tetramethyldisilane were used as monomers;[88] however, the polymers based on them had low molecular weights, 2400 and 10 000, as could be deduced from GPC data. The polyarylketone obtained from 4,4′-dichlorobenzophenone rapidly formed a precipitate (its molecular weight was as low as 1700). An alternative pathway for the synthesis of polyarylketone from polyketimine with subsequent hydrolysis of the ketimine groups has been proposed:[88]





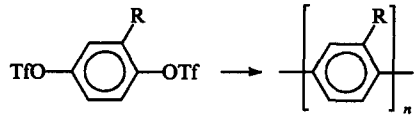


The polymer carrying ketimine groups is more readily soluble than its benzophenone analogue and has an inherent viscosity of 0.25 dl g^{-1} (when the synthesis is performed in *N*-methylpyrrolidone, the viscosity can amount to 0.36 dl g^{-1}).

Thus, the use of Ni^0 complexes has made it possible to obtain in some cases high-molecular-weight polymers from monomers carrying electron-acceptor substituents provided stringent conditions of the synthesis are observed.

b. Homopolycondensation of bistriflates

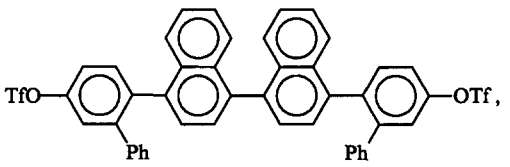
Ni^0 complexes are ideal catalysts for the homopolycondensation of aromatic substituted bistriflates.[94,95]



R = Ph, COOMe, Bu^t.

The reaction was carried out with Ni^0 prepared *in situ* in the presence of excess Zn. It should be noted that the degree of polymerisation of polyphenylenes with phenyl, carboxymethyl, and *tert*-butyl substituents is different,[90] reaching 15, 30–47 and < 14, respectively. It may be inferred from these data that with triflates the molecular weight was the highest when monomers carrying electron-acceptor substituents were used.

One serious pitfall of this method is that the coupling of monomers can proceed in a 'head-to-tail' and 'head-to-head' manner, resulting in polymers with irregular structures. In this respect, the application of symmetrical monomers seems to be more expedient. Thus, the synthesis of the following monomer:



has been described.[91]

Homopolycondensation of this monomer resulted in an oligomer with DP = 7–8 (GPC) with a 33%–35% yield. The oligomer appeared to be nonconjugated due to the non-coplanarity of the benzene nuclei; however, it can be transformed into a conjugated form by intramolecular cyclisation resulting in the formation of triphenylene or perylene structural fragments.

IV. Synthesis of heterocyclic polyarylenes

There is an ample body of evidence concerning the synthesis of low-molecular organic compounds by cross-coupling of halogen derivatives of thiophenes, pyridines, *N*-substituted pyrroles, quinolines, benzotriazoles, ferrocene,[96] and even halonucleosides with the use of Ni and Pd catalysts.[97] Attempts have been made to apply this methodology to the synthesis of heteroaromatic polyarylenes (especially, of conducting systems of the polythiophene type).[79,98–107]

Electrochemical methods or oxidation are used for obtaining heteroaromatic polymers; however, these techniques do not give, with a few exceptions,[108] regular structures.

By contrast, the cross-coupling reaction catalysed by transition-metal complexes allows for regio-specific interactions between the monomers, and correspondingly, the synthesis of polyheteroarylenes of a strictly defined structure. This approach was very extensively used in the synthesis of poly-2,5-thiophenes (to a lesser degree, poly-2,5-selenophene,[109] poly-2,5-pyrroles and related model oligomers).

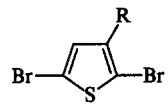
Cross-coupling reactions proved to be very effective in the synthesis of polythiophenes. In addition to the reproducible method for the synthesis of high-molecular-weight poly-2,5-thiophene, other procedures were elaborated for the synthesis of substituted poly-2,5-thiophenes and individual oligomers containing up to 7 cycles. As early as 1980, Lin[98] and Yamamoto[99]

described the polycondensation of 2,5-dibromothiophene and demonstrated the advantages of nickel catalysts over palladium ones in the synthesis of polythiophene.

Polycondensation cross-coupling aimed at the synthesis of heterocyclic polyarylenes developed along the three main lines: (i) the use of Grignard reagents and their further interaction with heterocyclic halides in the presence of Ni^{II} complexes; (ii) the use of stoichiometric quantities of Ni^0 complexes; (iii) the use of Ni^0 complexes synthesised *in situ* in the presence of reducing agents.

Poly-2,5-(thiophene) and its methyl derivatives have been obtained [98,99,102,103] in the following way: first, Grignard reagents were synthesised from the dibromides in the presence of a stoichiometric amount of Mg. They were subjected to polycondensation in the presence of catalytic amounts of a $NiCl_2$(bipy) complex in THF (first approach). The resulting product was poorly soluble in organic solvents (22%). The soluble fraction had a molecular weight, $\bar{M}_n$ = 1370.

In more recent studies,[106,107] the following substituted dibromothiophenes were used:



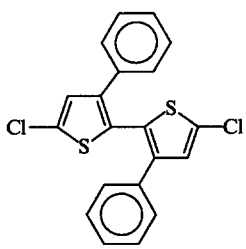
R = $C_{12}H_{25}$, Bu^n, n-C_6H_{13}, $(OCH_2CH_2)_nOCH_3$ (n = 1, 2) etc.

In both of the studies cited the monomer of the AB type was first obtained: to this end, one bromine atom was substituted by the MgBr group in the presence of the catalyst, Ni(dppp)Cl_2. The experimental conditions were such that the maximum molecular weight, $\bar{M}_w$, reached 71 000 (DP = 160). In this case, the yield of the 'head-to-tail' polymer amounted to 99%.

Yamamoto [79] suggested to use the Ni^0 – Ni(COD)$_2$ complex in the presence of Ph_3P or bipy for the preparation of substituted (R = C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$, CN) and non-substituted polythiophenes (second approach). The molecular weight of polythiophene with R = C_6H_{13} was 52 000 ($\bar{M}_w$, light scattering) and 190 000 for the samples obtained after 16 and 48 h, respectively.

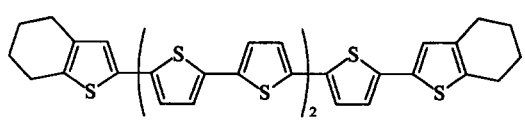
Ueda et al.[100] described the synthesis of poly-3-phenyl-2,5-thiophene based on a chloro-substituted monomer using catalytic amounts of Ni^0 complexes in the presence of reducing agents (third approach).

A symmetrical monomer with two thiophene groups has been recommended [111] for the synthesis of polythiophene.



This route precludes the formation of a polymer having an irregular structure. The inherent viscosity of the polymer was rather high rising to 0.23 – 0.25 dl g^{-1}.

Recently Bauerle [112,113] has described the synthesis of several intriguing oligothiophenes, such as the heptamer:

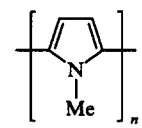


which is a compound of choice for electrochemical studies. It is noteworthy that analogous oligothiophenes were earlier obtained by other methods.[114–116]

As far as oligo- and poly-pyrroles are concerned, despite the considerable interest of investigators in these compounds (in the context of materials technology), only a small number of them have been synthesised with the use of the polycondensation cross-coupling method.

Thus, Kovacic [117,118] reports on the synthesis of phenyl- and benzyl-substituted poly-*N*-methyl-2,5-pyrroles from the corresponding 2,5-dibromopyrroles. After conversion into the corresponding bifunctional Grignard reagents, these pyrroles entered into the polycondensation reaction catalysed by Ni^{II}(acac) in the quantities exceeding the stoichiometric ones. The resulting oligomers were partly soluble in organic solvents but had rather low molecular weights (according to the residual bromine content).

A wide variety of oligomeric unsubstituted poly-*N*-methyl-2,5-pyrroles have been synthesised and fully characterised in the course of detailed studies carried out by Kaufman:[119]

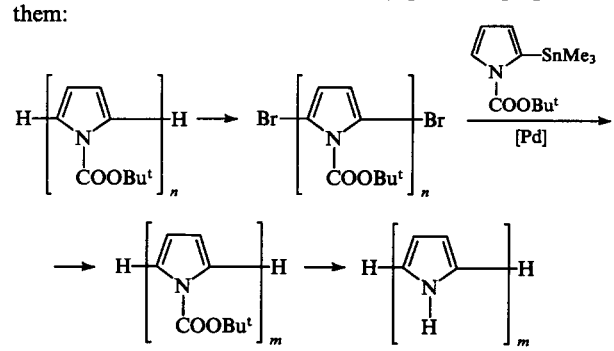


n = 2, 6, 8, 16.

It is to be mentioned, however, that the presence of methyl groups at the nitrogen atoms in the pyrrole rings decreases sharply the conductivity of polypyrroles. However, in the above syntheses only *N*-substituted pyrroles could be used, since the unprotected pyrrole is unstable (its sensitivity to even trace amounts of oxidants is well known). Therefore, the progress in the synthesis of conducting polypyrroles could be achieved if the problem of the monomer stability is solved.

The best solution of this problem is the use of *N*-substituted pyrroles provided the protecting group can be removed if required.[118,119] In this case, polycondensation of monomers results in protected oligomers and polymers, which can be converted into poly-2,5-pyrroles at the final stage of the reaction. *tert*-Butoxycarbonyl was used as the protecting group, since it decomposes completely to form CO_2 and isobutene,[120] favours an increase in the solubility of intermediate oligomers and polymers and thus facilitates their processing and analysis; it is also an electron acceptor, and, as a consequence, demonstrates a stabilising effect.

Below is given a scheme of the synthesis of the corresponding substituted oligopyrroles and of oligopyrroles prepared from them:



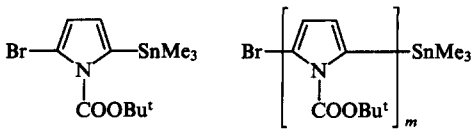
n = 1, 3, 5, 7; $m = n + 2$.

Bromination of *N-tert*-butoxycarbonylpyrrole (n = 1) has been carried out according to Gilow.[121] The dibromide thus obtained [122] reacted with two equivalents of a monotin derivative of *N-tert*-butoxycarbonylpyrrole [51] to give a trimer. Bromination of the trimer at the both terminal α-positions and its repeated reaction with the organotin derivative resulted in further elongation of the chain to yield a pentamer. This pentamer was then repeatedly introduced into the chain growth cycle and so on. The resulting oligomers were fully characterised by spectroscopic methods.[123] The crystal structure of some of these compounds was established by X-ray analysis.[1]

Heating of each of these polymers at 160–180 °C led to the elimination of the protecting COOBu^t-groups resulting in a series of unprotected oligopyrroles with $m = 3,5,7,9$. According to ^{1}H and ^{13}C NMR data, the deprotection was almost complete: the content of residual COOBu^t-groups did not exceed 4%. The longest pyrrole oligomer known thus far was terpyrrole. It is of note, however, that unprotected oligopyrroles are very unstable compounds, which form gels even at low temperatures; their treatment must be carried out in the absence of air.

The application of Pd-catalysed polycondensation to polypyrrole synthesis is coupled with certain difficulties, which are not still resolved. The attempts to synthesise polypyrroles under conditions of the Suzuki reaction (Pd-catalysed interaction of dihalides with diboronic acids) were unsuccessful, because in the case of pyrrole the electron-rich heteroatom easily loses its functional groups. For example, heating of *N-tert*-butoxycarbonylpyrrole-2-boronic acid in the biphasic toluene/Na_2CO_3 system for 24 h at 50 °C (in the absence of other components of the cross-coupling reaction and catalysts) resulted in a 50% loss of the $B(OH)_2$ groups, which thus determines the inapplicability of these compounds in the polycondensation reaction.[124, 125]

Therefore, an attempt has been made to prepare oligomers based on other monomers. To this end, monomers of the AB-type containing the trimethylstannyl group instead of $B(OH)_2$ have been synthesised:

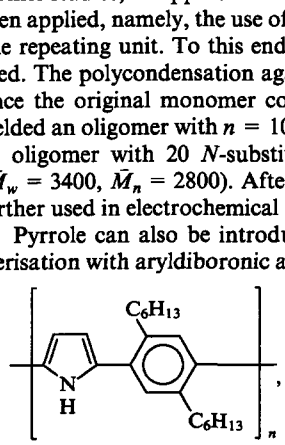


19 **20** ($m = 3$)

Studies of cross-coupling of compounds of this type have shown that monomers **19** and **20** are quite stable.[50]

According to liquid chromatography data, polycondensation of the monomer **19** yields only the oligomers with $n = 3-4$. To elucidate the reason for the low DP of these products, the lowest oligomers were isolated from the mixture and their structure was elucidated. It was found that they contain Me- and $SnMe_3$-groups as terminal groups rather than Br- and $SnMe_3$-groups as could be expected for the systems obtained by the interaction of the above monomers. The attempts to prevent the undesirable termination of the chain by varying the reaction conditions have failed. In further studies, an approach well-known in polycondensation has been applied, namely, the use of monomers containing more than one repeating unit. To this end, the terpyrrole monomer **20** was used. The polycondensation again proceeded with difficulty, but since the original monomer contained three structural units, it yielded an oligomer with $n = 10$. Fractionation of a mixture gave an oligomer with 20 *N*-substituted pyrrole rings in the chain ($\bar{M}_w = 3400$, $\bar{M}_n = 2800$). After deprotection, this oligomer was further used in electrochemical and optical-spectroscopic studies.

Pyrrole can also be introduced into the reaction of copolymerisation with aryldiboronic acid. The copolymer



was obtained by the interaction of the substituted aromatic diboronic acid with dibrominated protected pyrrole followed by thermal deprotection.[126] The resulting product had a rather high molecular weight, $\bar{M}_w = 17\,000-20\,000$.

* * *

It may be inferred from the above that the polycondensation cross-coupling employing transition-metal complexes as catalysts allows one to synthesise soluble carbo- and hetero-chain polyarylenes of a strictly defined structure.

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