Synthesis of novel bis- and polyarylene ethynylenes by cross-coupling catalyzed by palladium complexes

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A novel carborane-containing compound with ethynyl groups, 1,2-bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane, was synthesized. Cross-linking with 4-iodo- and 4,4′-diiododiphenyl ethers catalyzed by Pd complexes afforded the model bis-arylene ethynylenes and the corresponding polymers. The introduction of a carborane nucleus into the structure of the model compounds and polymers was shown to render these systems soluble.

Key words: polyarylene ethynylenes; diethynyl carborane-containing compound; cross-coupling reactions.

Cross-coupling catalyzed by transition metal complexes with the formation of a C—C bond serves as an efficient method for synthesizing numerous organic compounds including polyphenylenes, polyarylene vinylenes, and polyarylene ethynylenes. Growing interest has been expressed in this method over recent years because many of the polymers mentioned, especially the polymers with different side substituents, cannot be synthesized by any other method.

Polyarylene ethynylenes are polymers that can be the basis for the preparation of photo-conductive or electroconductive materials due to their ability to form charge-transfer complexes. They were previously synthesized[1—5] by cross-coupling between diethynyl compounds and aromatic dihalides or aromatic dicarboxylic acid chlorides[1] in the presence of palladium complexes. Most of the polymer systems described are insoluble in organic solvents due to the rigidity of the main chain and high crystallinity. The only exceptions were polymers with bulky side aliphatic substituents[4] soluble in toluene up to 3 g L^{-1}.

As has been stressed in several works (*e.g.*, see Ref. 5), the growth of chains stopped due to rapid precipitation of the polymers; for this reason, high-molecular polymers were not obtained. Dibromides, the most readily accessible compounds, were predominantly used as the dihaloarylenes. On the other hand, iodo-derivatives were significantly more active both in organic cross-coupling reactions[6,7] and in polymer synthesis[1] than bromo-derivatives. Polycondensations with diiodides can be carried out at temperatures not exceeding 100 °C rather than at 120—140 °C as with dibromides.[2,5] In the latter case, the possibility of polymerization of ethynyl groups themselves increased.[8]

The purpose of the present work was to synthesize a new diethynyl carborane-containing monomer and to study the possibility of its interaction with 4,4′-diiododiphenyl ether in order to obtain soluble polyarylene ethynylenes, since the carborane nucleus is known to increase the solubility of polymer systems.[9]

4,4′-Diiododiphenyl ether (**A**), which was used as the starting diiodoaromatic compound for the synthesis of the polymers, as well as 4-iododiphenyl ether (**B**), were prepared by direct iodination of diphenyl ether in an oxidating medium by the previously described procedure.[10]

The novel carborane-containing compound, 1,2-bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane (**1**), was prepared from **B** according to Scheme 1.

The initial steps of the reaction for the preparation of 1,2-bis[4-(4′-acetylphenoxy)phenyl]-*o*-carborane, the monomer for the synthesis of polyphenylenes by polycondensation, have been described by us previously.[11] The interaction of a diacetyl compound with PCl_5 in benzene afforded a chlorinated intermediate which was further dehydrochlorinated in the presence of sodium amide. The yield of compound **1** was 21 %. We also tried to use other dehydrochlorinating agents. However, when KOH in dimethylsulfoxide was used, the yield of **1** was less than 5 %, while using an alcoholic solution of an alkali or an aqueous solution of an alkali in the presence of an alcohol and phase transfer catalysts resulted in destruction of the carborane nucleus.

The method of dehydrochlorination in the presence of phase transfer catalysts afforded good results (40 % yield) when the product of interaction of 4,4′-diacetyldiphenyl ether with PCl_5 in the synthesis of the second

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†Deceased.

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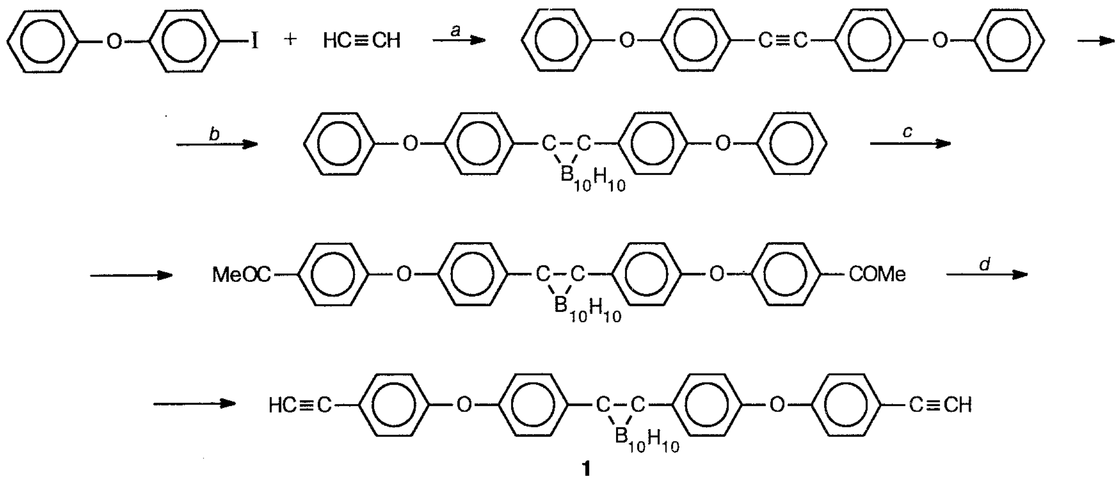
Scheme 1



Reagents: *a* — $PdCl_2(Ph_3P)_2$, CuI, Et_2NH; *b* — $B_{10}H_{14}$, $PhNMe_2$; *c* — MeCOCl, $AlCl_3$, NO_2Me; *d* — 1) PCl_5, 2) $NaNH_2$, NH_3

diethynyl monomer, 4,4′-diethynyldiphenyl ether (**2**), was dehydrochlorinated.

According to Scheme 2, the model bis-arylene ethynylenes were synthesized on the basis of diethynyl compounds **1** and **2** and 4-iododiphenyl ether (**B**).

The properties of the compounds synthesized are given in Table 1.

The synthesis was carried out in the presence of $PdCl_2(Ph_3P)_2$ (1 mol. %), the most widely used catalyst for reactions of this type, and 1 mol. % CuI, which was added as a promoter. In addition, 5 mol. % of triphenylphosphine and a small amount (5—6 mol mol^{-1}) of triethylamine (Et_3N) as an acceptor of HI and promoter of Pd^{II} reduction into Pd^0 were added. The reaction was carried out for 4 h at 100 °C in DMF. Under these conditions, the products of the cross-coupling of iodo- and ethynylaromatic groups, rather than of ethynylaromatic groups with each other, were predominantly formed.

Scheme 2

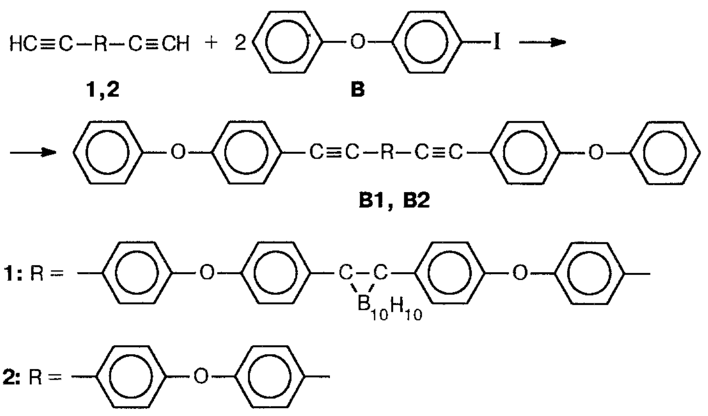
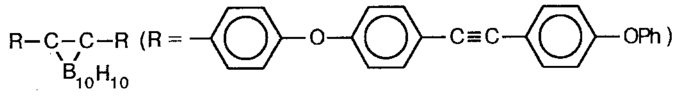
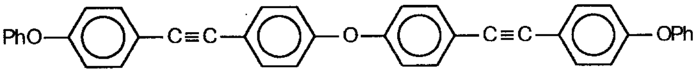
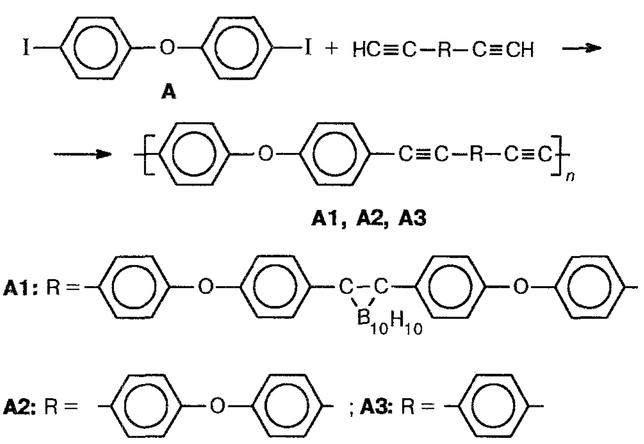


Table 1. Condensation of 4-iododiphenyl ether (**B**) with 1,2-bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane (**1**) and 4,4′-diethynyldiphenyl ether (**2**) (4 h, 100 °C, DMF)

Compound		Yield (%)	M.p./°C	$\frac{\text{Found}}{\text{Calculated}}$ (%)		
				C	H	B
	(**B1**)	33	83—85	$\frac{73.58}{75.00}$	$\frac{5.12}{5.09}$	$\frac{12.74}{12.50}$
	(**B2**)	81	207—210	$\frac{86.69}{86.64}$	$\frac{4.48}{4.69}$	—

Scheme 3



Although the yield of **B1** was not high (33 %), TLC did not reveal any compounds except **B1** and the original reagents. Compound **B1** is readily soluble in many organic solvents, *e.g.*, choloroform, DMF, *etc.*

The yield of compound **B2** was 81 %. It was completely insoluble both in organic solvents and in sulfuric acid, unlike 1,2-bis(4-phenoxyphenyl)acetylene[11] which has one acetylenic group and is readily soluble in benzene, chloroform, and DMF.

The synthesis of polymers was carried out according to Scheme 3.

The polymers were prepared on the basis of ether **A** and diethynyl compounds and mainly under the conditions used for bis-aryl ethynylenes, but at different temperatures and in different solvents, as well as in the presence of Et_2NH or Et_3N. The properties of polymers incorporating no carborane nuclei are given in Table 2.

Polymer **A3a** was prepared in Et_2NH at 20 °C, that is, under conditions used for the synthesis of substituted acetylenes, in a high yield.[12] The polymer rapidly precipitated from the solution. It has a very low molecular weight, *i.e.*, 670 (see Table 2). Increasing the reaction temperature to 100 °C and performing the synthesis in DMF resulted in an increase in the yield of the polymer and in an insignificant increase (up to 820) in its molecular weight (polymer **A3b** in Table 2). It is worth noting that the molecular weight of a polymer with a similar structure prepared from 4,4′-dibromodiphenyl ether under the conditions for the synthesis of polymer **A3b** was only 550 (see Ref. 5).

Like polymer **A3b**, polymer **A2**, which was synthesized from 4,4′-diethynylphenyl ether and 4,4′-diiododiphenyl ether at 100 °C in DMF, precipitated from the solution 5–10 min after the addition of a promoter (CuI). Its molecular weight (2400) was several times higher than that of polymer **A3b** (see Table 2). A polymer with similar structure, whose molecular weight was not determined, was prepared earlier[2] on the basis of 4,4′-dibromodiphenyl ether, and it was also insoluble.

Carborane-containing polymers were prepared under different conditions and, as above, using the catalytic system $PdCl_2(Ph_3P)$–CuI–Ph_3P–amine. The elemental composition was calculated based on the molecular weight found and assuming that the polymer contains one terminal iodo-group. The replacement of every third acetylene group in the macromolecule by a carborane nucleus resulted in a dramatic change in the properties of the polymers formed. All of them, as well as the model compound **B1**, were readily soluble in amide solvents, and some of them were soluble in chloroform.

Polymer **A1a**, which was prepared at 20 °C in benzene in the presence of Et_2NH, did not precipitate from the solution but it had rather a low molecular weight, *i.e.*, 1040. Its IR spectrum contained bands at 830, 1500, and 1600 cm^{-1}, which are related to the aromatic groups, a band at 1250 cm^{-1} related to the ether groups, and a band at 2600 cm^{-1} characterizing the B–H vibrations of the carborane nucleus.[9] It should be noted that the bands characterizing the acetylene groups of the main chain (2200 cm^{-1}) did not appear in the IR spectra of polymers **A1** and **A2** synthesized by us.

Polymer **A1b** synthesized in DMF at 100 °C had a rather high molecular weight, 5500, but destruction of the carborane nucleus occurred at this temperature, judging by the shift of the band at 2600 cm^{-1} in the IR spectrum. This led to a decrease in the thermal stability

Table 2. Polycondensation of 4,4′-diiododiphenyl ether (**A**) with 4,4′-diethynyldiphenyl ether (**2**) or 1,4-diethynylbenzene (**3**) (reaction time 4 h)

Polymer	Solvent	T_{exp}/°C	Yield (%)	Molecular weight*	T_g/°C	T_1**/°C	Found/Calculated (%) C	H	I
A2	DMF + Et_2NH	100	82	2400	245	450	<u>82.75</u> 82.89	<u>4.69</u> 4.00	<u>5.36</u> —
A3a	Et_2NH	20	66	670	230	380	<u>70.23</u> 72.90	<u>3.63</u> 3.47	<u>19.10</u> —
A3b	DMF + Et_2NH	100	98	820	250	390	<u>75.50</u> 75.82	<u>3.77</u> 3.93	<u>15.68</u> —

* Calculated from an elemental analysis for I, assuming that a molecule contains one terminal iodo-group.

** T_1 is the temperature at which 10 % weight loss is observed; determined by DTGA.

Table 3. Polycondensation of 4,4′-diiododiphenyl ether (**A**) and 1,2-bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane (**1**)

Polymer	Solvent (Amine)	T_{exp}/°C	Yield (%)	η_{red}/dL g^{-1} (25 °C, DMF)	$\bar{M}_n^a$ ($\bar{M}_w^b$)	T_g/°C	T_1^c/°C	Found / Calculated^d (%)			
								C	H	B	I
A1a	Benzene (Et_2NH)	20	50	0.06	1040	140	700	64.79 63.97	4.94 4.32	12.39 13.70	8.97 12.21
A1b	DMF (Et_2NH)	100	80	0.10	(5500)	200	480	—	—	12.59 15.20	0.5 2.31
A1c	*N*-methyl-pyrrolidone (Et_3N)	100	40	0.07			1000	—	—	15.09 —	13.64 —
A1d	DMF (Et_3N)	100	50	0.05	1100		670	—	—	13.59 13.84	12.19 11.15
A1e	THF (Et_3N)	50	65	0.06		145	600	63.99 61.11	4.74 4.12	13.67 13.09	9.00 15.80

[a] Ebullioscopic data obtained in chloroform.

[b] Sedimentation data obtained in *N*-methylpyrrolidone.

[c] T_1 is the temperature at which a 10 % weight loss is observed; determined by DTGA.

[d] Calculated from molecular weight data assuming that a molecule contains one iodo-group.

of the polymer: in this case, a 10 % weight loss was observed at significantly lower temperatures than with polymer **A1a** (Table 3). In contrast, the glass transition temperature (T_g) of polymer **A1a** with molecular weight 1060 was 60° lower than that of polymer **A1b** since the glass transition temperature still depends on the molecular weight at such low values of the latter.

Since the carborane nucleus in model compound **B1** was not destroyed in the presence of Et_3N, the synthesis of polymers **A1c—A1e** was carried out in the presence of this amine in *N*-methylpyrrolidone, DMF, and THF. The band at 2600 cm^{-1} in the IR spectra of these polymers did not shift. Therefore, the carborane nucleus did not decompose under these conditions. Polymers **A1c—A1e** were obtained in moderate yields (40—65 %) and had rather low molecular weights, that is, in fact they were oligomers. Judging from DTGA, they lost not more than 10 % of the weight when heated to 600 °C in the air.

Thus, using a catalytic cross-coupling reaction we could synthesize soluble oligoarylethynylenes based on a new monomer, and in one case rather a high molecular weight was reached. It seems likely that in order to prepare the polymers with high molecular weights one should use dihaloarylenes with electron-unsaturated bridging groups rather than a 4,4′-diiododiphenyl ether with an electron-donating oxygen group. This will be done in the future work.

Experimental

IR spectra were recorded on a UR-20 spectrometer. ^{1}H NMR spectra were obtained on a Bruker WP-200-SY instrument in $CDCl_3$. Thermomechanical curves were obtained on a Tsetlin's instrument for thermomechanical tests. Thermogravimetric analyses were carried out on MOM derivatograph (Hungary).

4,4′-Diiododiphenyl ether (A) and 4-iododiphenyl ether (B) were prepared by direct iodination of diphenyl ether in an oxidative medium.[10] For **A**: m.p. 139—140 °C (*cf.* Ref. 13: m.p. 140—141 °C). For **B**: m.p. 43 °C (*cf.* Ref. 14: m.p. 48 °C).

1,2-Bis[4-(4′-ethynylphenoxy)phenyl]-*o*-carborane (1). A mixture of 20 g (35 mmol) of 1,2-bis[4-(4′-acetylphenoxy)-phenyl]-*o*-carborane[11] and 15 g (36 mmol) of PCl_5 was dissolved in 100 mL of unh. C_6H_6 and boiled for 8 h. The organic phase was separated, washed with water, dried with $CaCl_2$, and concentrated. The product was dissolved in 30 mL of a mixture of unh. Et_2O and C_6H_6. The solution was added dropwise to sodium amide in 300 mL of NH_3 at −33 to −40 °C. The reaction mixture was stirred at this temperature for 4 h, then the organic phase was separated, and the ethynyl compound was extracted with hexane. The yield of compound **1** was 21 %; m.p. 157—158 °C. IR, ν/cm^{-1}: 3300 (—C≡CH); 2100 (C≡C); 2600 (B—H). ^{1}H NMR, δ: 2.7 (s, —C≡CH). Found (%): C, 67.08; H, 5.44; B, 20.07. $C_{30}H_{28}O_2B_{10}$. Calculated (%): C, 68.18; H, 5.30; B, 20.45.

4,4′-Diethynyldiphenyl ether (2): m.p. 74—75 °C (*cf.* Ref. 2: m.p. 75—76 °C).

Dichlorobis(triphenylphosphine)palladium was obtained as described earlier.[6]

Diethylamine and triethylamine were distilled over sodium.

Dimethylformamide and *N*-methylpyrrolidone were distilled over P_2O_5 and kept over freshly calcined molecular sieves.

1,4-Diethynylbenzene (3): m.p. 94—95 °C (*cf.* Ref. 15: m.p. 95 °C).

Bis-arylene ethynylenes B1 and B2 were obtained by the interaction of 4-iododiphenyl ether with diethynyl compound (2 : 1, mol mol^{-1}) in the presence of 1 mol. % of $PdCl_2(Ph_3P)_2$, 1 mol. % of CuI, 2 mol. % of Ph_3P, and not less than 6 mol. % of Et_3N in DMF at 100 °C. IR, ν/cm^{-1}: 710, 830, 1500, 1600 (Ar—H); 1250 (C—O—C); in the spectrum of **B1**: 2600 (B—H).

The polycondensation was carried out according to the general procedure: 0.4 g (0.78 mmol) of monomer **1**, 0.32 g (0.78 mmol) of 4,4′-diiododiphenyl ether, 1.6 mg of $PdCl_2(Ph_3P)_2$, 5 mg of Ph_3P, 0.6 mL of Et_3N, and 2 mL of *N*-methylpyrrolidone were placed into a flask equipped with a stirrer and an argon inlet and outlet. The mixture was heated with stirring until dissolution of the reagents, then 1.6 mg of CuI was added. The reaction was carried out for 4 h at 100 °C. The polymer was precipitated with MeOH, washed with MeOH, dilute HCl, water, again MeOH, and dried *in vacuo* at 60 °C.

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