

Synthesis of new aryl and hetaryl dibromides and diiodides, the monomers for preparation of polyarylene ethynylenes

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Dibromides and diiodides with quinoxaline, phenylimidazole, and hexa- or penta-phenylarylene fragments were synthesized from dihalotolans obtained from chloral. Oligoarylene ethynylenes were synthesized by the reaction of the monomers with equimolar amounts of diethynyl aromatic compounds in the presence of the Pd^{II} complex. Oligomers with imidazole and hexa(penta)arylbene cycles are soluble in amide organic solvents and their reduced viscosities do not exceed 0.09 dL g⁻¹.

Key words: chloral; dihalotolans; dihalobenzils; quinoxaline; substituted phenylimidazoles; dibromocyclopentadienone; dibromohexaphenylbenzene; dibromopentaphenylbenzene; oligoarylene ethynylenes.

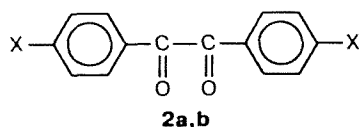
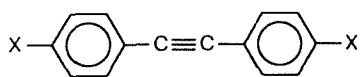
Cross-coupling catalyzed by transition metal complexes (Pd and Ni)¹ is one of the new methods for the synthesis of polyheteroarylenes and polyarylene ethynylenes, polymers with a polyconjugated structure.

Synthesis of polymers is usually based either on reactions of aromatic dibromides (diiodides) with bis-acetylenes,^{2,3} diboric acids⁴ or their esters,⁵ and bis(tri-alkylstannyl) compounds⁶ (the reactions mentioned are catalyzed by Pd complexes), or on homocondensations of aromatic or heterocyclic dichlorides (dibromides) in the presence of Ni complexes.⁷

The polycondensation cross-coupling allows one to synthesize a large number of different polymers with bulk groups in the main or side chain. The presence of such groups determines the solubility of polymers, which is important not only for their further conversion but mainly for the removal of the restriction for the growth of a macromolecular chain.

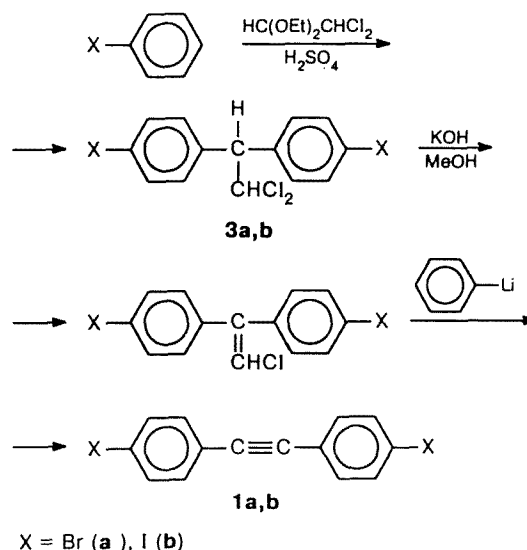
This work is devoted to the synthesis of heterocyclic and branched aromatic dibromides or diiodides. In most cases, the synthesis of monomers is based on the usage of chloral or dichloroacetal in initial steps of the synthesis.

The main intermediate products for the synthesis of the monomers mentioned are 4,4'-dihalotolans (**1a,b**) and 4,4'-dihalobenzils (**2a,b**), where X = Br (**a**) or I (**b**).



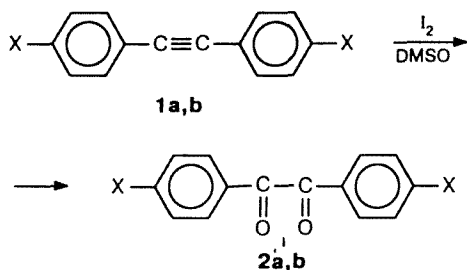
Earlier⁸ compounds **1a,b** were synthesized according to Scheme 1. The yields of 4,4'-dibromotolan **1a** and 4,4'-diiodotolan **1b** obtained from the corresponding diaryldichloroethane **3** were ~75 % and 35 %, respectively.

Scheme 1



Oxidation of dihalotolans **1a,b** readily affords dihalobenzils **2a,b** (Scheme 2).⁹

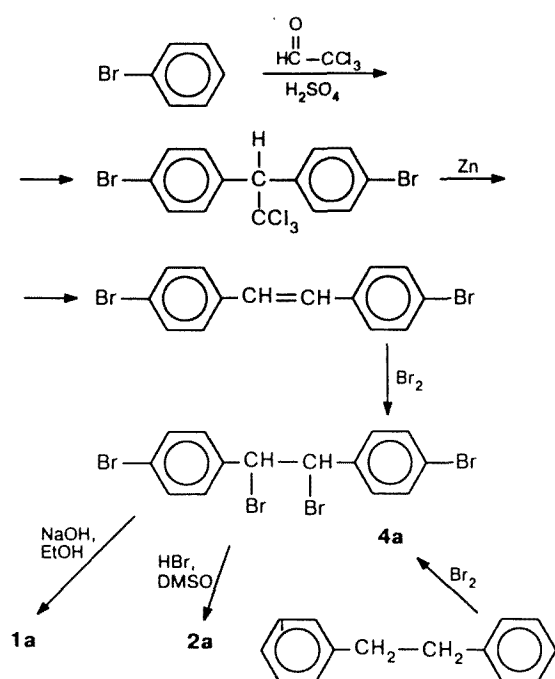
Scheme 2



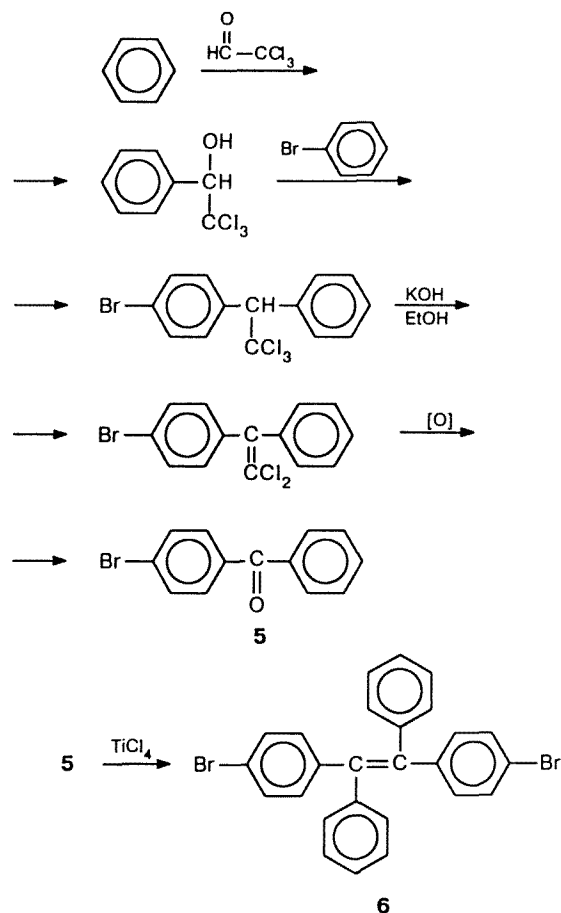
We have developed a simpler scheme for the synthesis of compounds **1** and **2** (Scheme 3). Bromo(or iodo)benzene was treated with chloral, the product was reduced with zinc, and bromostilbene obtained was converted to 1,2-bis(4-bromophenyl)-1,2-dibromoethane (**4a**) with bromine or to the corresponding diiodo derivative **4b** with iodine. Compound **4a** can also be readily obtained by the direct bromination of dibenzyl. Bis(bromophenyl)dihaloethane **4a** was converted to dibromotolan **1a** or dibromobenzil **2a** by dehydrobromination with alcoholic alkali or by oxidation, respectively. The yield of **1a** at the final step of the synthesis was 84 %.

Using chloral, 4-bromobenzophenone (**5**) can be synthesized. The treatment of the latter with TiCl_4 affords an interesting monomer, 1,2-bis(4-bromophenyl)-1,2-diphenylethylene (**6**) (Scheme 4). Although compound **5** is obtained in four steps, all the reactions proceed in good yields (up to 90 %).

Scheme 3



Scheme 4



Benzene was treated with a large (5–10-fold) excess of chloral, the resulting product was introduced into the reaction with bromobenzene (1 mmol), the intermediate was subjected to dehydrochlorination, and the product that formed was oxidized. The yield of olefin **6** after the treatment of bromobenzophenone **5** with TiCl_4 was 84 %. This reaction was carried out by the procedure previously described for benzophenone.¹⁰

Scheme 5

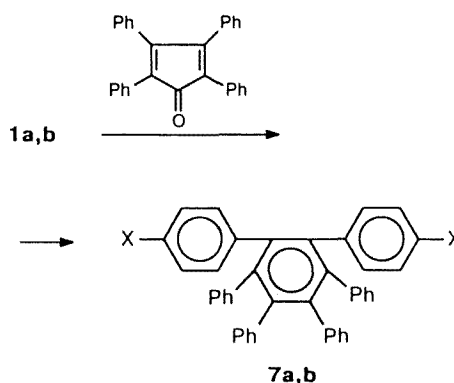


Table 1. Characteristics of the synthesized monomers

Com- pound	Yield (%)	M.p. /°C	IR, v/cm ⁻¹	Found — (%)				Molecular formula
				Calculated	C	H	Br (I)	
1a	84	182—183		49.83	2.22	47.94		C ₁₄ H ₈ Br ₂
				50.00	2.08	47.92		
1b	80	241—243*		38.80	2.09	59.07		C ₁₄ H ₈ I ₂
				39.07	1.87	59.02		
2a	93	224—226	1680	46.25	2.22	44.17		C ₁₄ H ₈ O ₂ Br ₂
				46.40	2.22	44.14		
2b	78	255—256	1680	36.52	1.85	54.66		C ₁₄ H ₈ O ₂ I ₂
				36.39	1.74	54.93		
6	84	198—199		63.50	3.77	32.39		C ₂₆ H ₁₈ Br ₂
				63.69	3.70	32.60		
7a	85	345—347		72.77	4.00	23.16		C ₄₂ H ₂₈ Br ₂
				72.84	4.08	23.08		
7b	88	>350		64.04	4.02	31.92		C ₄₂ H ₂₈ I ₂
				64.14	3.59	32.27		
8a	92	197—199	1620—	55.02	2.87	36.36	5.86	C ₂₀ H ₁₂ N ₂ Br ₂
			1640	54.58	2.74	36.32	6.36	
8b	85	187—188	1620—	45.11	2.17	47.64	5.04	C ₂₀ H ₁₂ N ₂ I ₂
			1640	44.97	2.26	47.52	5.25	
9	92	240—242	1670	64.08	3.39	29.61		C ₂₉ H ₁₈ OBr ₂
				64.23	3.34	29.47		
10	81	245—247		70.56	3.51	25.80		C ₃₆ H ₂₃ Br ₂
				70.26	3.77	25.97		
11	84	312—314	3300	55.62	3.20	35.24	6.12	C ₂₁ H ₁₄ N ₂ Br ₂
				55.50	3.08	35.06	6.17	
12	87	342—344	3300,	50.82	2.73	32.06	8.21	C ₂₁ H ₁₃ N ₃ O ₂ Br ₂
			1540	50.50	2.61	31.62	8.42	

* Literature data:⁸ m.p. 240—241 °C.

Dibromosubstituted hexaarylbenzene **7** was obtained by Diels—Alder reaction¹¹ by refluxing compound **1** in benzophenone with tetraphenylcyclopentadienone (tetracyclone) (Scheme 5) in 85 % yield (Table 1).

The synthesis of monomers from 4,4'-dihalobenzil **2** was carried out by the three methods (Scheme 6).

1. The reactions of dibromide **2a** and diiodide **2b** with *o*-phenylenediamine¹² afford 2,3-di(4-bromophenyl)-quinoxaline (**8a**) and 2,3-di(4-iodophenyl)quinoxaline (**8b**), respectively, in >80 % yields.

2. The reaction of compound **2a** with dibenzylketone^{13—15} affords dihalosubstituted tetracyclone **9**. The reaction of the latter with tolan and phenylacetylene gives hexaarylbenzene **7** and pentaarylbenzene **10** (in 81 % yield), respectively.

3. The treatment of compound **2a** with aldehydes in the presence of ammonium acetate and acetic acid¹⁶ results in the formation of substituted bromoimidazoles **11** and **12** in >80 % yield.

Oligoarylene ethynyls based on synthesized dibromo-containing monomers were obtained by the procedure described earlier^{2,3} using *p*- and *m*-diethynylbenzene and 4,4'-diethynyldiphenyl ether as co-monomers (Scheme 7). The reactions were carried out in dimethylacetamide (DMAA) at 110 °C for 6 h, the catalytic system was the following: PdCl₂(Ph₃P)₂ (1—2 mol. %) + CuI (3 mol. %) + Ph₃P (5—6 mol. %) + Et₃N (5—6 mol. %).

Oligomers **13—18** (Table 2) were precipitated from the reaction solutions and did not further dissolve in any organic solvents. The average polymerization degrees did not exceed 4 judging from the content of bromine. The previously obtained² polymer with a structure very close to that of **13** was insoluble and probably had a low molecular weight.

Introduction of *m*-phenylene and diphenyl ether groups instead of *p*-phenylene ones did not effect the solubility of polymers **16—18** containing quinoxaline cycles.

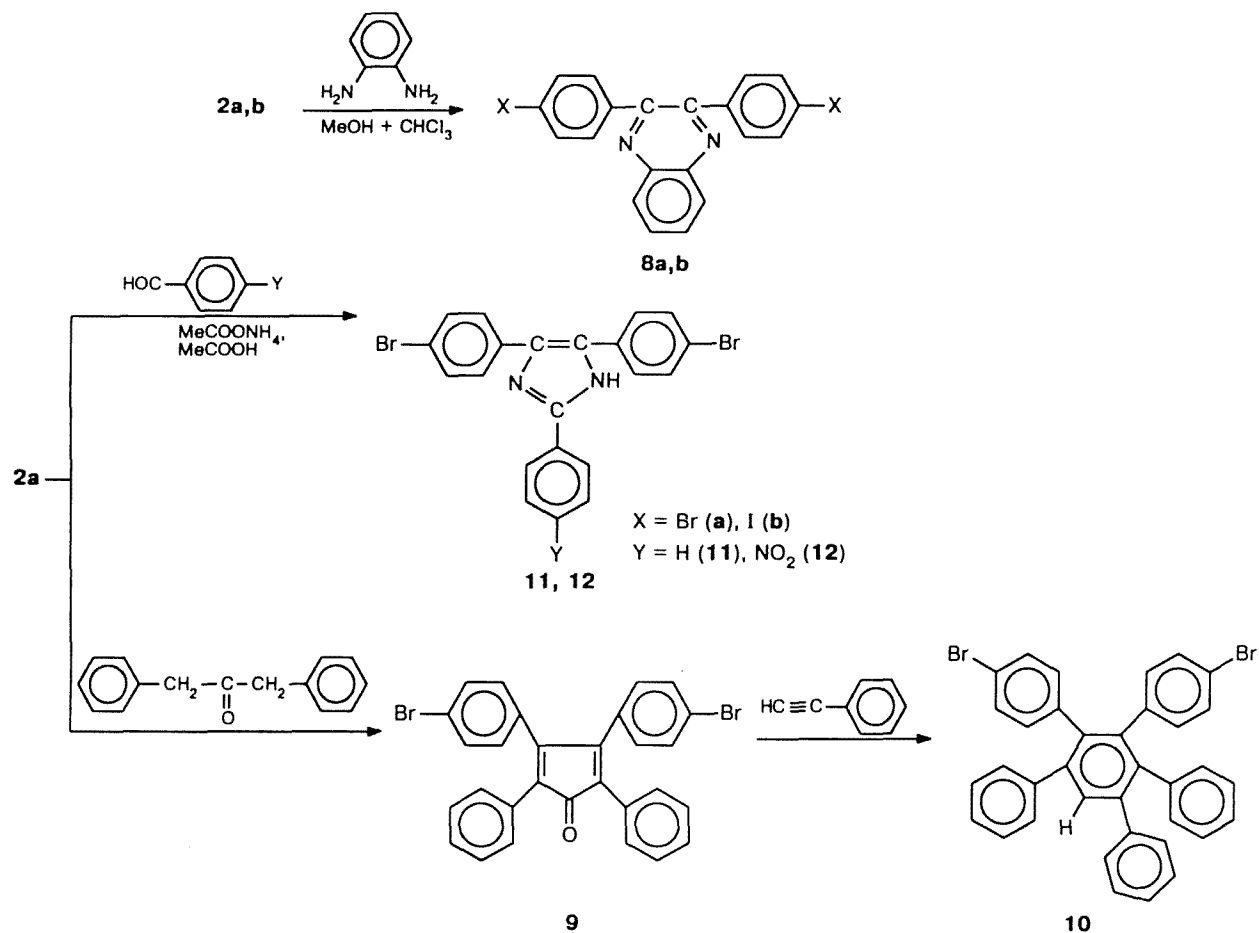
We supposed that soluble oligophenylene ethynylene vinyls may be obtained from monomer **6**. However, they also appeared to be insoluble though their molecular weight was somewhat higher than that of the oligomers described previously, judging from the content of bromine.

Oligomers with imidazole and hexa(penta)arylbenzene cycles **19—22** are readily soluble in DMF and other amide solvents. The viscosities of the polymers obtained to date are not very high (η_{red} up to 0.09 dL g⁻¹, see Table 2), but studies along this line are in progress.

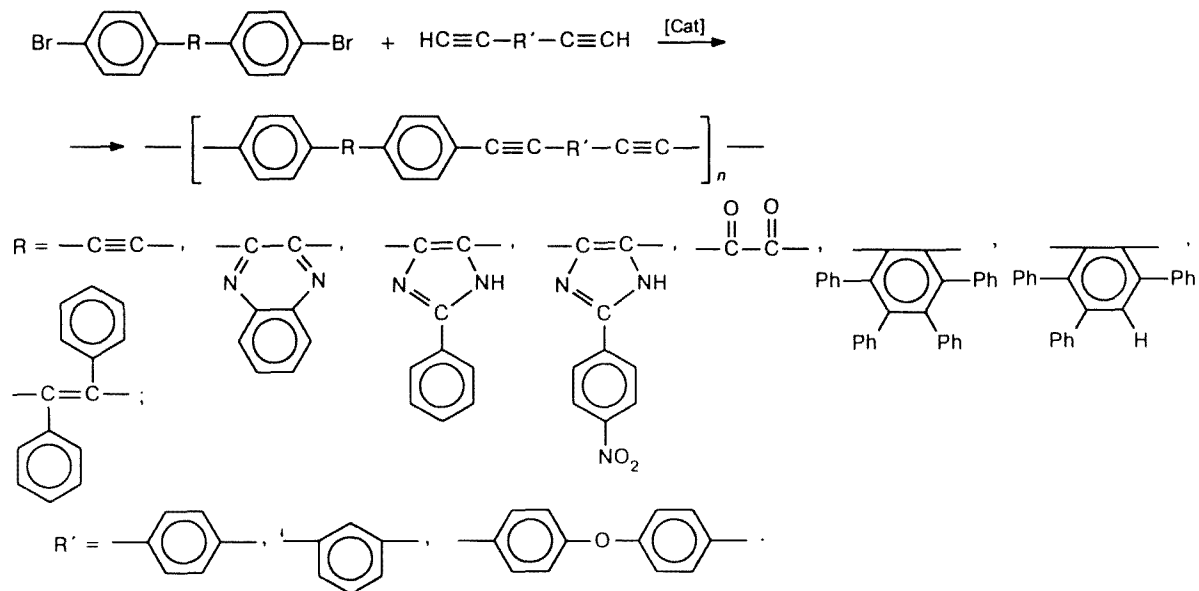
Experimental

IR spectra were obtained on a UR-20 instrument in KBr pellets. We used 4-bromobenzophenone (m.p. 80—82 °C),

Scheme 6



Scheme 7



1,2-diphenylethane (m.p. 50–53 °C), tetraphenyl cyclopentadienone (m.p. 217–220 °C), *o*-phenylene diamine (m.p. 103–105 °C), dibenzylketone (m.p. 32–34 °C), benzaldehyde (n_D^{20} 1.5450), and *p*-nitrobenzaldehyde (m.p. 105–107 °C) of "pure" grade. 1,2-Bis(4-bromophenyl)-1,2-dibromoethane (m.p. 245–247 °C) was synthesized by the previously described procedure.¹⁷

4,4'-Dibromotolan (1a). A solution of 1,2-di(4-bromophenyl)-1,2-dibromoethane (**4a**) (20 g, 0.04 mol) in abs. ethanol (50 mL) was added to a solution of NaOH (19 g) in abs. ethanol (300 mL). The solution was refluxed for 2 h, cooled, and poured into water. The precipitate formed was filtered off, washed with ethanol, dried, and crystallized from dioxane to afford **1a** in 84 % yield, m.p. 182–183 °C (cf. Ref. 8: m.p. 182–184 °C).

4,4'-Dibromobenzil (2a). *A.* A mixture of compound **1a** (2.1 mmol), I₂ (0.25 g, 1 mmol), and DMSO (5 mL) was heated at 155 °C for 6 h with stirring. Then the reaction mixture was cooled and poured into a 1 % solution of Na₂S₂O₃ (20 mL). Yellow crystals that precipitated were filtered off, washed with water, dried, and crystallized from dioxane to give **2a** in 93 % yield, m.p. 224–226 °C.

4,4'-Diiodobenzil (2b) was obtained by a similar procedure in 78 % yield, m.p. 255–260 °C (cf. Ref. 18: m.p. 254–256 °C).

4,4'-Dibromobenzil (2a). *B.* DMSO (1500 mL) and HBr (150 mL) were added to compound **4a** (150 g, 0.3 mol) and the reaction mixture was slowly heated to 110 °C with stirring. At this temperature the starting compound was completely dissolved. The reaction was carried out at 110 °C for 9 h. After 0.5 h, the precipitation of **2a** started. The reaction mixture was then cooled, and the yellow crystals that precipitated were filtered off, dried, and crystallized from dioxane to afford **2a** in 80 % yield, m.p. 225–226 °C (cf. Ref. 19: m.p. 224–226 °C).

1,2-Di(4-bromophenyl)-1,2-diphenylethylene (6). TiCl₄ (5 mL) was added to a solution of 4-bromobenzophenone (**5**) (7.80 g, 0.03 mol) in THF (200 mL) at –10 °C. Then a suspension of zinc powder (5.9 g, 0.09 mol) in THF (100 mL) was added dropwise to the reaction mixture at the same temperature. The reaction mixture was heated to boiling, refluxed for 5 h

with stirring, and then cooled. The resulting solution was filtered, and the filtrate was poured into water and extracted with ether. The organic layer was washed with water, dried, and the solvents were distilled off. The product was crystallized from *n*-butanol to afford **6** in 84 % yield, m.p. 198–199 °C (cf. Ref. 20: m.p. 198–199 °C).

1,2-Di(4-bromophenyl)-3,4,5,6-tetraphenylbenzene (7). Melted benzophenone (5 g) was mixed with compound **1** (1.9 g, 5.65 mmol) and tetracyclone (1 g, 2.6 mmol) at 50 °C. The mixture was heated at vigorous boiling (305 °C) for 1 h. Diphenyl ether (1 g) was then added to the reddish-brown reaction mixture. The crystals formed were filtered off, washed with benzene to a white color, then with methanol, and dried *in vacuo*. The product was crystallized from diphenyl ether (the residual solvent was extracted with ethanol) to afford **7** in 85 % yield, m.p. 345–347 °C.

1,2-Di(4-bromophenyl)quinoxaline (8a) was synthesized by the previously described procedure,¹² m.p. 197–199 °C (cf. Ref. 12: m.p. 198–199 °C).

1,2-Di(4-iodophenyl)quinoxaline (8b) was synthesized by the same procedure,¹² m.p. 187–188 °C (cf. Ref. 12: m.p. 188–189 °C).

2,3-Di(4-bromophenyl)-1,4-diphenylcyclopentadienone (9) was synthesized by the previously described procedure,¹⁵ m.p. 240–242 °C (cf. Ref. 15: m.p. 240–242 °C).

2-Phenyl-4,5-di(4-bromophenyl)imidazole (11). Glacial acetic acid (100 mL) was added to a mixture of compound **2a** (5 g, 13.6 mmol) and ammonium acetate (10.5 g, 135 mmol) in argon flow. The reaction mixture was heated to 100 °C, then benzaldehyde (1.4 mL, 13.6 mmol) was added dropwise, and the solution was refluxed at 118 °C for 5.5 h. The mixture was cooled and poured into water, and the precipitate formed was filtered off, washed with ethanol, dried, and crystallized from *n*-butanol to afford **11** in 84 % yield, m.p. 312–314 °C.

2-Nitrophenyl-4,5-di(4-bromophenyl)imidazole (12) was synthesized by the similar procedure in 87 % yield, m.p. 342–344 °C.

Table 2. Properties of the obtained polymers

Compound	Main polymer unit	Yield (%)	Found/Calculated* (%) Br	η_{red} /dL g ⁻¹ (DMF)
13		57	10.65 11.75	Insoluble
14		72	12.67 10.33	The same
15		74	8.35 8.22	The same

Table 2 (continued)

Compound	Main polymer unit	Yield (%)	Found Calculated* (%) Br	η_{red}^{DMF} /dL g ⁻¹
16		72	<u>11.78</u> 7.87	Insoluble
17		69	<u>12.01</u> 8.99	The same
18		70	<u>11.63</u> 7.87	The same
19		58	<u>16.99</u> 8.99	0.09
20		60	<u>13.21</u> 8.57	0.07
21		65	<u>11.21</u> 5.74	0.08
22		68	<u>16.09</u> 6.45	0.06

* Calculated for $n = 4$.

1,2-Di(4-bromophenyl)-3,4,6-triphenylbenzene (10). Compound **9** (2 g, 3.69 mmol), phenylacetylene (0.94 g, 9.23 mmol), and *o*-dichlorobenzene (15 mL) were put into a two-necked flask with stirrer and reflux condenser and the mixture was refluxed for 32 h. The reaction solution was then cooled and poured into ethanol (100 mL), and the precipitate formed was filtered off and crystallized from *n*-butanol to afford **10** in 81 % yield, m.p. 245–247 °C.

Synthesis of oligomers (general procedure). Compound **8a** (0.4416 g, 1 mmol), 4,4'-diethynylbenzene (0.1004 g, 1 mmol), PdCl₂(Ph₃P)₂ (0.0021 g), Ph₃P (0.0042 g), DMAA (1.5 mL), and Et₃N (0.5 mL) were put into a flask with stirrer and an inlet and outlet for argon and the mixture was heated to 110 °C. Then CuI (0.0021 g) was added and the reaction mixture was stirred for 6 h at this temperature. The mixture was cooled and poured into methanol (10 mL), and the precipitate formed was filtered, washed twice with water, 5 M HCl, water, and methanol, and dried.

This study was financially supported by the International Science Foundation (Grant MKX 300) and the Russian Foundation for Basic Research (Project No. 95-03-08112a).

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Received July 21, 1995;
in revised form November 17, 1995