A Convenient Preparative Method of Dibromoterphenyl and Bis(bromophenyl)diene Monomers Using Zirconacyclopentadienes

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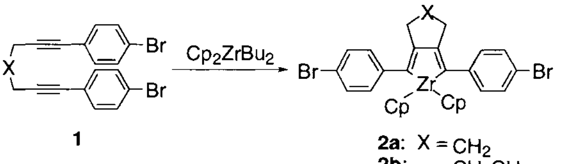
Zirconacyclopentadienes prepared from 4,4'-dibromodiphenyldiynes or 1-(4'-bromophenyl)-1-alkynes reacted with dimethylacetylene dicarboxylate in the presence of CuCl afforded polyphenylene monomers which contain three benzene rings. Hydrolysis, chlorination with NCS, or allylation of the zirconacyclopentadienes gave a variety of polyphenylenedienylene monomers. Polymerization of these monomers using the system $NiCl_2(PPh_3)_2$ (cat.)/Zn produced the corresponding polymers.

Recently we have found and developed the carbon-carbon bond formation reactions of zirconacyclopentadienes such as allylation[1] and aromatic ring formations[2] in the presence of CuCl. During the course of our further study in this area, we found that bromophenyl-substituted alkynes or diynes provided polyphenylene or polyphenylenediene monomers by our reactions. In this paper we would like to report the preparation of polyphenylene or polyphenylenediene monomers which contain one substituted aromatic ring or one substituted diene with two bromophenyl moieties at both ends.

Oligomers or polymers containing zirconacyclopentadienes have been reported. For example, the spiro cores thiophene oligomers were prepared from zirconacyclopentadienes for molecular electronic devices.[3] Zirconacyclopentadiene polymers were prepared based on the reaction of polyynes with zirconocene (II) complex and followed by hydrolysis to afford poly(*p*-phenylenedienylene)s.[4] Although diynes were also reported to couple with Negishi reagent to give zirconacyclopentadiene polymers,[5] further chemical conversion led to low isolated yield of poly(*p*-phenylene) due to the poor solubility of polymer.[5e] One best way to solve this problem is to prepare monomers for polyphenylenes or polyphenylenedienylenes from zirconacyclopentadienes in advance.

The precursor **1** was prepared by the reaction of terminal diynes with *p*-bromoiodobenzene in the prescence of a catalytic amount of $Pd(PPh_3)_4$, CuI and triethylamine in THF at room temperature. Treatment of **1** with Cp_2ZrBu_2 led to the complete formation of zirconacyclopentadienes **2** (eq 1). Bromophenyl moeity was not reduced with Cp_2ZrBu_2, although it was shown that debromination of aromatic bromide proceeded under the similar conditions.[6]



(1)

1

2a: X = CH_2
2b: CH_2CH_2
2c: O

Reaction of **2** with dimethylacetylene dicarboxylate in the presence of CuCl at room temperature gave 4,4'-dibromo-*p*-terphenyl derivatives **3**,[2] **3a-c** showed symmetrical structures which contained two carboxylate groups at ortho position and bromophenyl groups at para position. The regiochemistry in **3a-c** was completely controlled because of intramolecular coupling of **1**. The monomer **3d** was prepared by intermolecular dimerization of 1-(4'-bromophenyl)-1-hexyne. This coupling was not regioselective and afforded three isomers in a ratio of 5:1:1 (Figure 1).

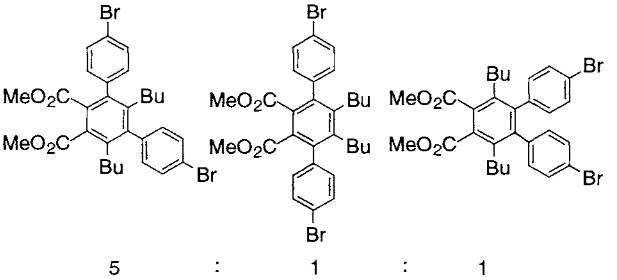
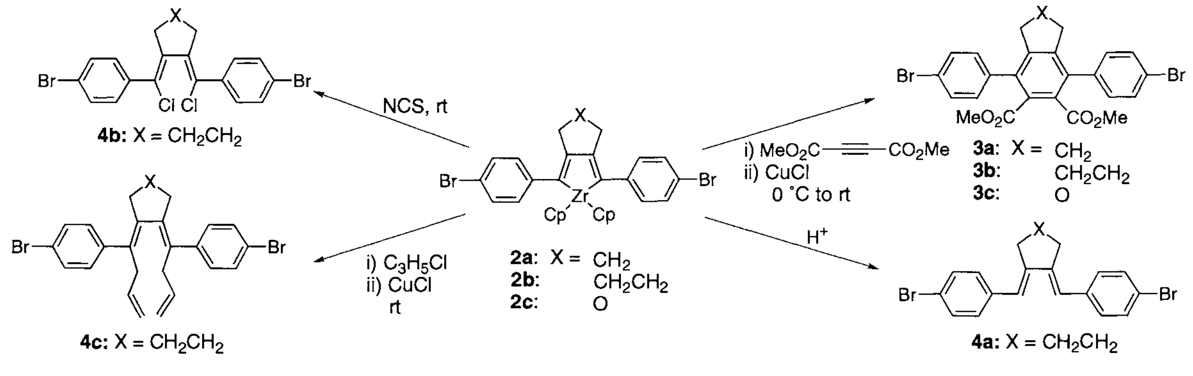


Figure 1. Isomers of **3d.**



Scheme 1. Preparation of monomers for polyphenylene and polyphenylenedienylene.

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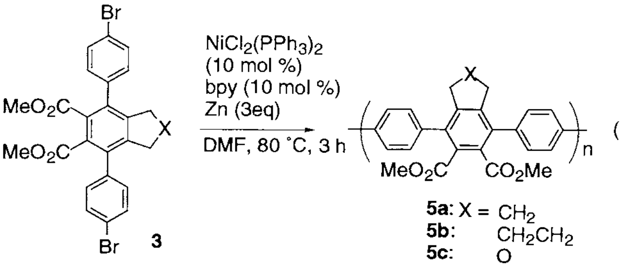
Functionallized polyphenylenedienylene monomers can also be obtained by the similar method. Hydrolysis and chlorination[7] of **2b** led to the isolation of 4,4'-dibromo-1,4-diphenyldiene and dichlorinated analogue in 72% and 75% yields, respectively. Treatment of **2b** with allyl chloride in the presence of CuCl resulted in the formation of **4c** (Scheme 1). It is noteworthy that a variety of polyphenylene and polyphenylenedienylene monomers can be obtained by a simple reaction sequence based on zirconacyclopentadienes **2**.

The typical experimental procedure for preparation of **3b** is described as follows: Dimethyl acetylenedicarboxylate (2 mmol) and CuCl (2 mmol) were added at 0 °C to a THF solution of zirconacyclopentadiene **2b** prepared *in situ* according to a known procedure.[8] The mixture was then warmed to room temperature and stirred for 6 h. After hydrolysis with 3 N HCl, purification using column chromatography on silica gel (hexane/Et_2O = 4/1) afforded **3b** as a pale yellow solid in 80% yield.

Polymerization of aryl halides using the nickel catalysts/Mg or Zn has been well documented.[9-10] In our case the use of zinc as reductant gave the best results. Treatment of monomers **3** with a catalytic amount of $NiCl_2(PPh_3)_2$ and bipyridine in the presence of zinc powder in DMF at 80 °C led to the formation of polyphenylenes **5**[10b] (eq 2).



(2)

The results of the polymerization of dibromoterphenyl monomers **3a-d** prepared here are shown in Table 1. All of the polyphenylenes were isolated from good to high yields. The molecular weights of **5** were determined by GPC and confirmed by elemental analyses except **5c**. Molecular weight of **5c** was calculated based on elemental analysis. There is no significant effect of the reaction time on the yield and the degree of polymerization (DP). Molecular weights of polyphenylenes obtained here were comparable to usual polyphenylenes.

Poly(*p*-diphenylenedienylene)s **6-8** were obtained from **4** in high yields by the same method described above (eq 3). The results of the preparation of poly(*p*-diphenylenedienylene)s are summarized in Table 2. The polymer **6** was isolated as a pale yellow-green solid. However, it was not soluble in organic solvents such as chloroform, THF and acetone. Molecular weight of **6** was calculated based on elemental analysis and showed an average DP of 11. The low average DP of **6** is due to the poor solubility. Functionalized poly(*p*-diphenylenedienylene)s **7** and **8** were obtained as pale yellow solids and showed better solubilities than **6** in chloroform. The molecular weights were determined by GPC and confirmed by elemental analyses. The average DP of these polymers are between 16 to 23. The average DP increased when two allyl groups were introduced.

Table 1. Preparation of polyphenylenes

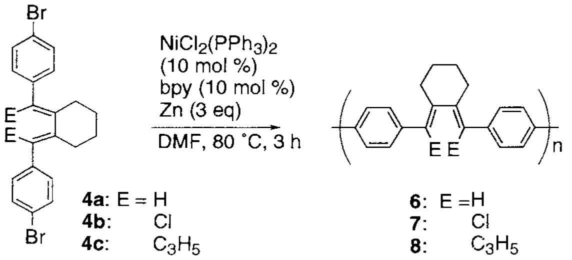
monomer	time/h	polymer	yield/%	Mn[a]	Mw	Mw/Mn
3a	3	**5a**	82	4750	5750	1.2
	24		85	4810	5850	1.2
3b	3	**5b**	75	6870	11700	1.7
	24		94	7510	13400	1.8
3c	3	**5c**	74	6700[b]	--	--
3d[c]	3	**5d**	78	5370	6760	1.3
	24		80	5150	6480	1.3

[a] Molecular weight were determined by GPC. [b] Molecular weight was determined by elemental analysis. [c] Mixture of three isomers.

Table 2. Preparation of poly(*p*-diphenylenedienylene)s

monomer	time/h	polymer	yield/%	Mn[a]	Mw	Mw/Mn
4a	3	**6**	93	3000[b]	--	--
4b	3	**7**	78	5600	11600	2.1
	24		67	5050	8360	1.6
4c	3	**8**	73	7860	14700	1.9
	24		80	6270	12500	2.0

[a] Molecular weight were determined by GPC. [b] Molecular weight was determined by elemental analysis.



(3)

In conclusion, zirconacyclopentadienes provided a convenient preparative method of monomers for polyphenylenes or polyphenylenedienylenes.

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