Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 46 (2005) 2533–2537

Tetrahedron Letters

Construction of benzene ring-layered polymers

Yasuhiro Morisaki and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received 25 January 2005; revised 11 February 2005; accepted 21 February 2005

Abstract—A simple and novel approach for synthesizing the benzene ring-layered polymers using [2.2]paracyclophane and xanthene skeletons was demonstrated. Palladium-catalyzed polymerization of pseudo-*p*-diethynyl[2.2]paracyclophane **1**, 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**, and ethynylferrocene **3** gave the corresponding polymers **4a**–**c**, which composed of 7–30 face-to-face benzene rings by changing the feed ratio of **1**–**3**.

In the field of organic compounds, the presence of cyclophane compounds, particularly those that consist of intramolecular face-to-face π-conjugated systems, has been acknowledged.[1] Among these, [*n.n*]paracyclophanes ($n = 2$ or 3) have the π-electron-cloud-overlapped structure, and such phanes are central to the study of cyclophane chemistry. A number of [*n.n*]paracyclophane derivatives have been prepared, and their unique structural and electronic properties resulting from characteristic interactions between the two cofacial π-electron systems have been investigated in detail.[1,2] On the other hand, few studies have been conducted on cyclophane-containing conjugated polymers;[3–6] further, the structures and properties of these polymers are limited because of their poor solubility in common organic solvents.[3–5] Recently, we reported the novel preparation and the physical properties of well-defined conjugated polymers[7] having cyclophane derivatives as key units, and the obtained polymers showed an extension of π-delocalization via the through-space and exhibited intense photo- and electroluminescence.

Since charge transfer through the organic material is achieved effectively via intermolecular π–π interaction between the conjugated systems, the incorporation of the compound with π-stacked benzene rings into the polymer backbone is expected to result in highly efficient charge hopping as well as energy transfer. Furthermore, recently there has been considerable interest in the construction of a molecular wire using rigid-rod π-conjugated oligomers in order to realize one of the most sophisticated molecular devices.[8,9] From the above mentioned, therefore, it is desirable that the molecular wire is constructed by using the π-electron cloud via the through-space conjugation rather than the sp or sp^2 bond via the through-bond conjugation.[10]

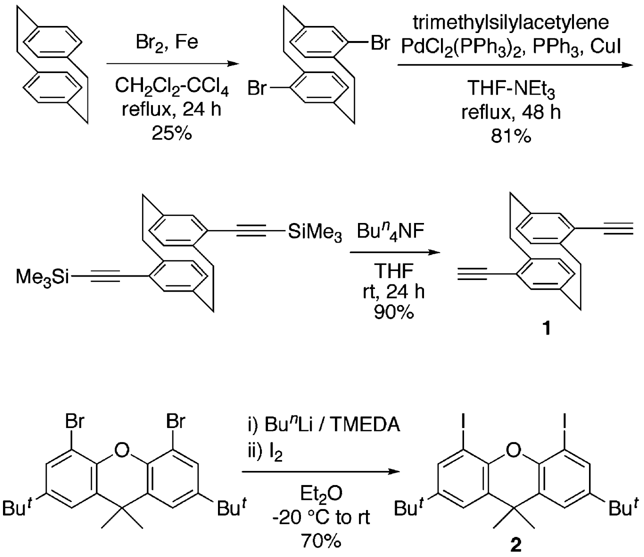
In this letter, we report a simple and novel process for the formation of the benzene ring-layered polymer, which consists of aligned benzene rings that face each other, by a palladium-catalyzed coupling reaction of pseudo-*p*-diethynyl[2.2]paracyclophane **1**[7f] with 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**.[11] Rotary motion of two aromatic rings attached to 1,8-position of naphthalene, biphenylene, xanthene, and so on, is restricted due to steric hindrance, and two aromatic rings having bulky units adopt a face-to-face structure. Rosenblum and co-workers reported the synthesis of the polymer having aligned metallocenes on the 1,8-position of the naphthalene skeleton by another approach, and investigated chemical, electrical, magnetic, and optical properties.[12] In this report, we focused on a novel construction of the molecular wires that are composed of layered benzene rings. The synthesis, characterization, and stereochemistry are discussed in detail.

The monomers pseudo-*p*-diethynyl[2.2]paracyclophane **1**[7f] and 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene **2**[11] were prepared as shown in Scheme 1. Polymerization of **1**, **2** and ethynylferrocene **3** proceeded smoothly in the presence of catalytic amounts of Pd(PPh$_3$)$_4$ and CuI in THF–NEt$_3$ for 48 h at 50 °C

Keywords: [2.2]Paracyclophane; Benzene ring-layered polymer; π–π Stacking; Through space; Molecular wire.

* Corresponding author. Tel.: +81 75 383 2604; fax: +81 75 383 2605; e-mail: chujo@chujo.synchem.kyoto-u.ac.jp

0040-4039/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2005.02.112

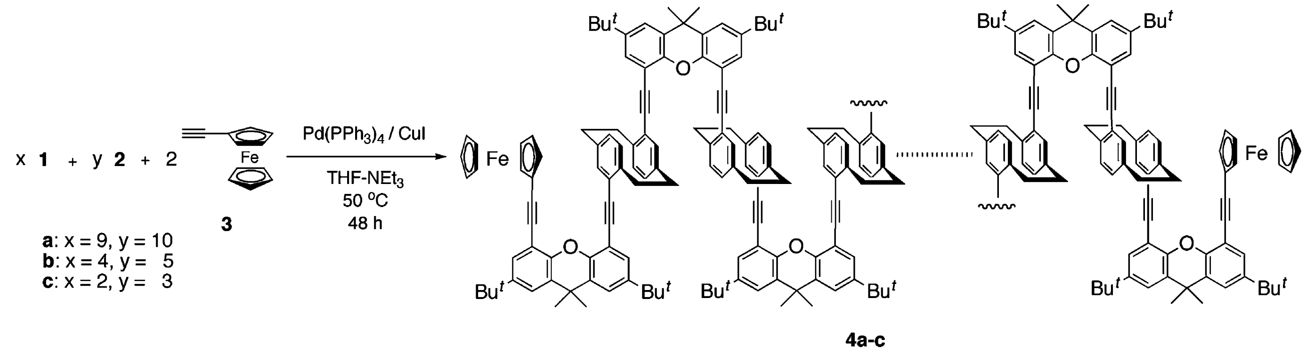


Scheme 1.

under N_2 atmosphere,[13] as shown in Scheme 2. Ethynylferrocene was added for end-capping the polymer termini. After the reaction, solution was concentrated and poured into a large amount of MeOH to obtain the corresponding polymers **4a–c** in good yields (89–96%); the results of this reaction are summarized in Table 1. The molecular weight was estimated by the ^{1}H NMR integral ratio between the protons of the terminal ferrocene group and those of the *t*-Bu group of the xanthene skeleton (Fig. 1(a)), and the results are also listed in Table 1. For example, the number-average molecular weight (M_n) of polymer **4a** obtained from run 1 was M_n = 9000, indicating that the number of cyclophane units incorporated into the polymer backbone is 15, that is, N = 32 benzene rings including two terminal cyclopentadienyl units of ferrocene are aligned.

The ^{1}H NMR spectra of (a) the benzene column **4a**, (b) the monomer **1**, and (c) the PPE-type [2.2]cyclophane-containing polymer prepared by us[7a] are shown in Figure 1. All signals in Figure 1a agree with the structure of the polymer **4a**. The number-average molecular weight (M_n) and the number-average of layered benzene rings (N), including two terminal cyclopentadienyl units of ferrocene were also calculated by assuming the ^{1}H NMR integral ratio (*t*-Bu protons vs ferrocene protons) as M_n = 9000 (calculated molecular weight = 5912) and N = 32 (Fig. 1a). In Figure 1a–c, the signals observed at 2.5–4.0 ppm were assigned to the bridged methylene protons of the [2.2]paracyclophane unit as shown in the square. The bridged methylene protons of polymer **4a** displayed highly broad and upfield-shifted signals (Fig. 1a), while those of the PPE-type polymer (Fig. 1c) were observed in the same region as those of monomer **1** (Fig. 1b). This result implies that the bridged methylenes of polymer **4a** are affected by the ring current of the benzene ring of the subsequent [2.2]paracyclophane unit.[15]

Contrary to our expectation, the UV–vis spectra of polymers **4a–c** were almost identical and exhibited absorption maxima at approximately 330 nm and higher energy absorptions at approximately 290 nm (Fig. 2), regardless of the number of layered benzene rings. On the other hand, it was reported that the absorption spectra of multi-layered cyclophanes exhibited bathochromic and hyperchromic effects as the number of the



Scheme 2.

Table 1. Synthesis of benzene ring-layered polymers **4a–c**

Polymer	Molar ratio[a]			Yield[b] (%)	Calcd.		Found[d]	
	1	**2**	**3**		M_n	N[c]	M_n	N[c]
4a	9	10	2	96	5912	20	9000	32
4b	4	5	2	96	3038	10	4900	16
4c	2	3	2	89	1888	6	2750	9

[a] 0.10 mmol of the monomer **2** was used.

[b] Isolated yield after reprecipitation.

[c] The number of the layered benzene ring including two terminal cyclopentadienyl units of ferrocene.

[d] Estimated by the ^{1}H NMR integral ratio.