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Easy synthesis of phenyl oligomers using a Ni complex

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Received 7th January 2004, Accepted 7th January 2004
First published as an Advance Article on the web 21st January 2004

In this work are described the syntheses of *p*-sexiphenyl and *p*-octiphenyl starting from 4-bromo-*p*-terphenyl and 4-bromo-*p*-quaterphenyl, respectively, by using a nickel complex in the presence of bipyridine with DMF as solvent. This type of synthesis was shown to give an improved yield as well as easy preparation and purification of these phenylene oligomers.

The study of semi-conducting polymers like poly(*p*-phenylene) (PPP), poly(*p*-thiophene) (PPT), poly(*p*-phenylene vinylene) (PPV) and polyaniline (PAn) has dramatically increased after the discovery of the high conductivity of doped polyacetylene (PA) by Shirakawa *et al.* in 1977.[1] However, the complexity of the polymer usually formed, hindered the completion of the study. Studies on model molecules, usually oligomers,[2–5] allow a good understanding of the characteristics of the corresponding polymer, since they possess a defined degree of polymerization and consequently uniformity.

But the key question is: from which size is the oligomer representative of the polymer? For PPP it is believed that these characteristics begin to be observed starting from *p*-quaterphenyl (oligomer with four aromatic rings), for the vibrational characteristics at least.

Another very important point in research using oligomers is their preparation, because of the high degree of purity required. There are a lot of methods in the literature proposed for the coupling of aromatic rings. Among the classical methods, are found the reactions of Grignard, Fittig, Ullmann or Wurtz, but these well known methods are not favorable for the synthesis of phenyl oligomers due to several limitations such as: low yield, drastic conditions of synthesis, tedious purification, non-reproduceable results and multiple step synthesis.[6–11] For example:

■ In the work developed by Cadê and Pilbeam[7] the butyllithium was reacted with 4-bromo-*p*-terphenyl in the presence of cobalt chloride and butyl bromide. In this synthesis the *p*-sexiphenyl, whose yield was not mentioned, was obtained after distillations, washing, extractions with hydrochloric acid, water and then benzene followed by sublimation. But, the yields mentioned for the products are given before final rigorous purification.

■ In 1964, Doss and Solomon[10] presented a *p*-sexiphenyl synthesis in which this oligomer was obtained with a yield of 1% after irradiation electrochemistry of the *p*-terphenyl at 320 °C for 14 hours.

■ Kovacic and Lange[12] synthesized *p*-sexiphenyl by chemical polymerization of *p*-terphenyl, using $AlCl_3/CuCl_2$ as a catalyst. The process, under optimised conditions, lead to a mixture of oligomers with 35% yield. However, although their UV-Vis absorption spectrum and melting points correspond to the literature values, the infrared absorption spectra present some shifted bands, for example the one corresponding to the C–H in-plane vibration is found at 811 cm^{-1} whereas it should be at 814 cm^{-1}, which could be due to a contamination of the obtained material.

The use of nickel complex to promote a C–C bond was extensively studied[13–17] in the case of dehalogenative condensation of dihaloaromatic compounds to give π-conjugated polymers in the presence of $Ni(COD)_2$. To avoid the above-described problems, in this work on the synthesis of phenylene oligomers, we have used this general method of C–C bond formation in the presence of nickel complex. We describe below the synthesis of *p*-sexiphenyl (**I**) and *p*-octiphenyl (**II**), using 4-bromo-*p*-terphenyl (**III**) and 4-bromo-*p*-quaterphenyl (**IV**) respectively (Fig. 1).

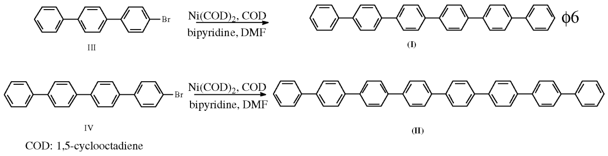

Fig. 1 Synthesis of *p*-sexiphenyl (**I**) and *p*-octiphenyl (**II**).

The synthesis of the monobromo compound is an important factor in the formation of the oligomers. The starting product should have only one bromine, located at the 4-position of the aromatic ring, in order to form the desired oligomer. The point in this type of synthesis is to avoid the insertion of more than one bromine. For *p*-terphenyl, the substitution of the first bromine atom at the 4-position happens rather easily, but the substitution of a second bromine in the 4′-position is more complicated.

In the case of *p*-quaterphenyl, the situation is quite different. The presence of a bromine atom at one of the extremities (4-position) is not able to hinder the substitution of the second bromine, because of the molecule length, therefore the final product results in a mixture of 4-bromo-*p*-quaterphenyl and 4,4′-dibromo-*p*-quaterphenyl. In the case of terphenyl even if there is, in the final product, the presence of 4,4′-dibromo-*p*-terphenyl it is always possible to separate the compounds by sublimation. For the quaterphenyl this is not so easy. When an certain quantity of dibromo compound is mixed with the monobromo, we observed that these two materials formed a composite crystal, preventing the separation of the two compounds. The solution was to reduce the ratio reactant : bromine (1 : 0.8), even if that results in a smaller yield of the desired compound. In this way, although the synthesis is incomplete and an amount of starting material (*p*-quaterphenyl) remains, it is easily recovered. The monobromo compound and a small quantity of dibromo product can be separated through sublimation.

The infrared spectra of these three compounds show important differences in the low-frequency range between 900 and 600 cm^{-1}. Strong absorption bands come from the out-of-plane (oop) bending of the C–H bonds. For *p*-quaterphenyl three bands can be seen at 823, 750 and 682 cm^{-1} (Fig. 2). When a bromine atom is inserted (4-bromo-*p*-quaterphenyl) a shift of the bands is observed (808, 762 and 687 cm^{-1}). However for a product with two bromines (4,4′-dibromo-*p*-quaterphenyl) the IR spectra show a strong band at 804 cm^{-1}. The intensity of this band is so strong, that it hides the others, only a small band appears at 822 cm^{-1} that could come from some unreacted *p*-quaterphenyl.

DOI: 10.1039/b400236a

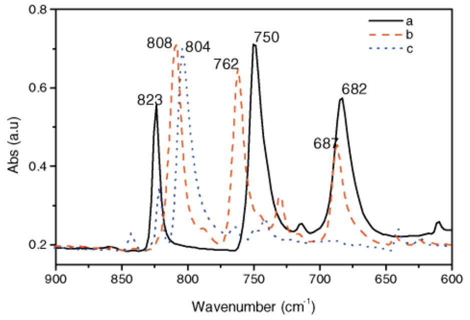

Fig. 2 Infrared spectra of (a) *p*-quaterphenyl, (b) 4-bromo-*p*-quaterphenyl and (c) 4,4′-dibromo-*p*-quaterphenyl (100 scans, 4 cm^{-1}).

In Fig. 3 the results of DSC show melting points of *p*-quaterphenyl, 4-bromo-*p*-quaterphenyl and 4,4′-dibromo-*p*-quaterphenyl. It can be seen that the values increase as a function of the quantity of bromine, 337 °C for the 4-bromo-*p*-quaterphenyl and 377 °C for the 4,4′-dibromo-*p*-quaterphenyl. The presence of only one endothermic peak for these two materials also proves the purity of the synthesized products.

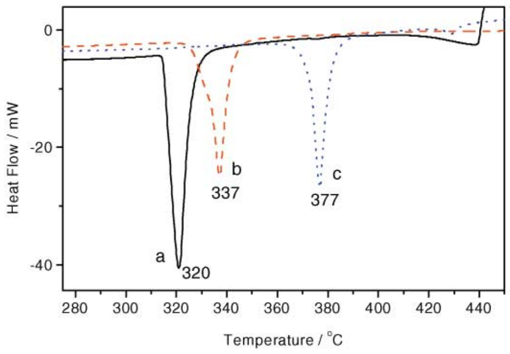

Fig. 3 DSC spectra of (a) *p*-quaterphenyl, (b) 4-bromo-*p*-quaterphenyl and (c) 4,4′-dibromo-*p*-quaterphenyl.

The *p*-sexiphenyl synthesized from monoterphenyl with the nickel compound is 100% pure and a sublimation step is not required because any unreacted material (*p*-terphenyl) and/or 4-bromo-*p*-terphenyl can be eliminated by washing with hot toluene and filtration. Because of this, the synthesis becomes an easy preparation, relatively fast without sublimation, which usually reduces the yield of the obtained oligomer.

During the synthesis it was possible to follow the change of coloration for the reaction mixture: from blue to yellow, when using a large quantity of catalyst. In the work developed by Yamamoto *et al.*[18] on the formation of biphenyl with Ni(COD)$_2$, they first saw a purple color (formation of Ni(BPY)(COD)), then red for a short time and a green solution (formation of NiBr$_2$(BPY)).

In the infrared and Raman spectra of *p*-sexiphenyl, all the bands show the same position and intensity as described for this phenylene oligomer obtained by electrochemical reaction after extensive purification.[19] This is a signature of the good purity of the obtained material. Besides, we could not see the characteristic bands of *p*-terphenyl (839, 745 cm^{-1}) or 4-bromo-*p*-terphenyl (818, 762 cm^{-1}) in the infrared spectrum. In the same way, a characteristic spectrum was also observed for *p*-octiphenyl, with the C–H out-of-plane vibrations located at 810 cm^{-1} for di-substituted rings and 762 cm^{-1} for mono-substituted rings, as already described in the literature.[20]

Yamamoto *et al.*[18] promote various reactions using Ni(COD)$_2$ as a catalyst to obtain biphenyl in order to determine the mechanism of C–C coupling of aromatic halides. They used an excess of phenyl bromine in the presence of 2,2′-bipyridine at 50–70 °C and the yields were in the range of 75–100%, using DMF as a solvent under argon or nitrogen. This polar solvent is suitable for C–C coupling reactions promoted by Ni(COD)$_2$ and was already used for reactions of polymers, but they did not used COD in excess to stabilize the catalyst. Semmelhack and co-workers[21] have reported similar dimerization of aryl halides using Ni(COD)$_2$ without addition of the auxiliary ligand (2,2′-bipyridine). However their yields were lower than those obtained by Yamamoto. In the case of the syntheses of *p*-sexiphenyl and *p*-octiphenyl, the reaction involved is more complicated due to certain factors such as the solubility of the used compounds and their lower reactivities. Because of this it is also necessary to use 1,5-(cyclooctadiene) to form the oligomers.[17]

The utilization of nickel complex with COD ligands and an excess of 2,2′-bipyridine and COD to promote a C–C bond was shown to be favorable for the synthesis of *p*-sexiphenyl and *p*-octiphenyl. The obtained oligomers are 100% pure after a simple washing, thus avoiding sublimation and tedious further purification.

Experimental

The Fourier Transform Raman Scattering spectra were recorded on a Bruker RFS100 spectrometer with an excitation wavelength (λ_{exc}) of 1064 nm. For infrared absorption spectra a Nicolet 20SXC with an Attenuated Total Reflection (ATR) accessory was used. The two measurements were obtained with a resolution of 4 cm^{-1}. The DSC measurements were carried out with a TG-DSC equipment model 111 from Setaram, in the temperature range 20–500 °C (5 °C min^{-1}) under argon.

All reagents were purchased from commercial sources (Aldrich or Fluka), without further purification except when specified. The 4 bromo-*p*-terphenyl (**III**) was prepared as described in the literature[22].

4-Bromo-*p*-quaterphenyl (**IV**): in a 50 mL three-necked flask, equipped with a pressure-equalizing dropping funnel, a reflux condenser and a stirring bar, were placed 1.008 g (3.29 mmol) of *p*-quaterphenyl and 0.13 mL (2.61 mmol) of bromine in 30 mL of 1,2-dichlorobenzene at 85 °C for 24 hours under argon. The solution was filtered at room temperature, washed with ethanol and dried. The material was sublimated in a four-zone oven, η 28%.

p-Sexiphenyl (**I**): inside the dry-box, in a 50 mL three-necked flask, a mixture of 1.11 g (3.59 mmol) of 4-bromo-*p*-terphenyl, 0.41 g (2.63 mmol) of 2,2-bipyridine, 0.61 g (2.22 mmol) of bis(1,5-cyclooctadiene)nickel(o) and 0.74 mL (6.85 mmol) of 1,5 cyclooctadiene was added to DMF (30 mL). The mixture was stirred at 70–75 °C for 40 h under argon, filtered, washed with water, HCl solution in ethanol for elimination of Ni^{2+} and then ethanol. After drying, the material was washed with hot toluene for elimination of eventual *p*-terphenyl and 4-bromo-*p*-terphenyl (η 34%).

For the *p*-octiphenyl (**II**) the method used was the same as that described above for *p*-sexiphenyl (**I**), but the temperature was set at 70–75 °C for 40 hours and the product was washed with boiling THF for elimination of eventual *p*-quaterphenyl and 4-bromo-*p*-quaterphenyl.

Acknowledgements

The authors thank Dr Claude Chevrot (Laboratoire de Physicochimie des Polymères et des Interfaces – LPPI – Université Cergy Pontoise – France) for very helpful discussion and suggestions. Laura O. Péres thanks the French “Ministère de la Recherche” for the financial support.

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