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# The Use of Suzuki Reaction to Form a New Electroluminescent Block Copolymer

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**Summary:** A new material from 4,4′-dibromo-*p*-quaterphenyl (PPP oligomer) and 9,9-dioctylfluorene-2,7-diboronic acid was easily synthesized by Suzuki reaction in good yield (84%). A complete characterization was done in order to compare the properties of the copolymer with its monomers. The material was readily soluble in organic solvents. The absorption as well as emission spectra presented red shifted compared to those from depart materials.

**Keywords:** block copolymer; PPP; quaterphenyl; Suzuki reaction; synthesis

## Introduction

The Suzuki reaction is a reaction which involves the junction of two carbon atoms in the presence of a palladium catalyst, between on one hand a compound containing a borate and on the other an organo-halide.[1–3] This reaction offers several additional advantages, since it is not affected by the presence of water and it tolerates a wide range of functional groups. Besides, the inorganic by-product of the reaction is no toxic and it can be removed easily from the reaction mixture, which turns out to be satisfactory not only in laboratory work, but also for industrial processes.

Polymerization reactions involving the Suzuki reaction have been shown to give nice results, mainly because of the absence of by-reactions. The difficulty arising in this type of synthesis is the formation of the boronic compounds, inducing difficulty in its analysis and/or separation.[4] As an alternative route to overcome this problem, several authors prepared the diesters of the boronic acids,[5,6] because they can be easily purified through chromatographic processes.

There are many polymeric materials synthesized by this technique like copolymers containing fluorene group. Many of these materials show good photoluminescence efficiency. The 9 position of the fluorene offers the ability to control interactions among chains through functionalization, cross-linking and plays a role on electrical and optical properties.[7] Another interesting material is poly(*p*-phenylene) (PPP) because of its potential optical applications with a band gap in the blue region and a good thermal stability combined with a high photoluminescence.[8,9] However this type of polymer is quite insoluble and it is believed that soluble oligomers containing four aromatic rings present almost the same characteristics as the polymer itself, at least concerning the vibrational properties.[10] The *p*-quaterphenyl can be used as laser dyes,[11] while the application most often claimed so far for poly(fluorene) was in light emitting diodes (LED).

In the present work we present the synthesis of a new alternating copolymer from 4,4′-dibromo-*p*-quaterphenyl (2) and 9,9-dioctylfluorene-2,7-diboronic acid (3) (Figure 1). The characterizations of this material were also done in order to understand its properties.

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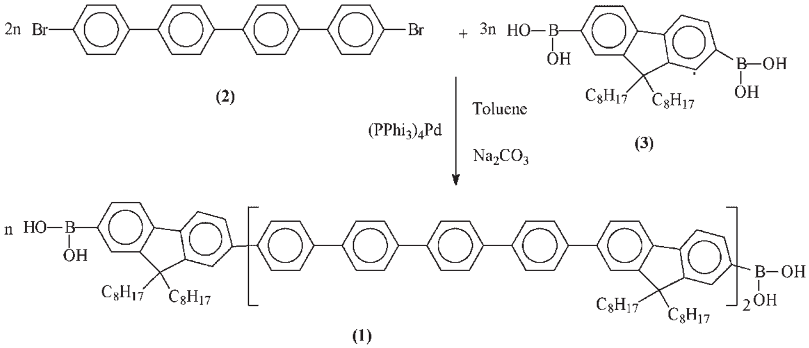

**Figure 1.**
Formation of block copolymer by polycondansation using Suzuki reaction.

## Experimental

### Starting Materials

All reagents were purchased from commercial sources (Aldrich or Acros) and used without further purification except when specified. The 4,4′-dibromo-*p*-quaterphenyl (2) was prepared as described in the literature.[10] The solvents for chemical reaction were dried under nitrogen.

### Characterization

$^1$H and $^{13}$C nuclear magnetic resonance spectra (200 MHz) were recorded on a Bruker DRX-500 spectrometer using deuterated chloroform (Aldrich) as solvent and tetramethylsilane as internal reference. FTIR spectra were performed on a Nicolet Avatar 320© spectrometer. Samples were dissolved in chloroform and cast on KBr plates and evaporated to dryness before collecting transmission spectra from 450 $cm^{-1}$ to 4500 $cm^{-1}$ at 4 $cm^{-1}$ resolution (32 scans). Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. Raman scattering spectra were recorded on a Bruker RFS100 spectrometer with an excitation wavelength $\lambda_{exc}$ set at 1064 nm. Wide-angle X-ray diffraction measurements were carried out on a D5000 Siemens diffractometer using Cu $K_\alpha$ line ($\lambda = 1.54$ Å) on polymer films in a conventional horizontal configuration using a scan rate of 2 °/min with 2θ ranging from 2 to 60°. The UV absorption spectra were collected on a Varian equipment model Cary 50. Samples were dissolved in chloroform and the solution was poured into a 10 mm square quartz cell. The transmission spectrum was collected from $\lambda = 200$ to 600 nm. The photoluminescence spectra (PL) in solution were determined using a Varian Eclipse fluorescence spectrophotometer. Samples were dissolved in chloroform and submitted to irradiation at the absorption maximum observed by UV spectroscopy and the emission spectra were collected accordingly. UV absorption and photoluminescence measurements were also done in solid-state. The material was dissolved in chloroform and the film was deposited by casting on a glass plate as substrate. The TG 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. The size exclusion chromatography (SEC) was done using the Agilent 1100 chromatographic system with refraction index detector, eluent THF 1mL/min 35 °C, two columns: pL gel mixed C and PL gel mixed B, polystyrene standards.

### Synthesis of Alternating Copolymer

0.502 g (1.05 mmol) of 9,9-dioctylfluorene-2,7-diboronic acid (Aldrich 96 %), 0.327 g (0.705 mmol) of 4,4′-dibromo-*p*-quaterphenyl, 0.012 g (0.01 mmol) of $P(Ph_3)_4Pd$ (Acros 99 %), were placed in a dry box with 15 mL of toluene and 7 mL of $Na_2CO_3$ solution

(2 M) under protection of argon. The materials were mixed in a three-necked flask, equipped with a pressure-equalizing dropping funnel, a reflux condenser attached to an argon bottle and a stirring bar for 24 hours in a dark place. After this period, the solution was filtrated and washed with toluene and water and dried with $MgSO_4$. The solvent was evaporated and a white solid was characterized as the copolymer (1). $\eta = 84\%$. $C_{135}H_{156}B_2O_4$: Calcd. C 86.97, H 8.43, B 1.16, O 3.43; Found C 83.57, H 8.68.

## Results and Discussion

The Figure 2 shows the $^1H$ NMR of the alternating copolymer and the monomers in deuterium chloroform. For the copolymer the following assignments are done: $\delta = 7.8–7.2$ (m, 22H, Ar-H); 1.98 (m, 4H, $CH_2$); 1.08 (s, 20H, $CH_2$); 0.81 (m, 6H, $CH_3$). In the $^1H$ NMR of the quaterphenyl, it's possible to observe the peaks at 7–7.8 ppm due to the aromatic rings. The NMR spectra of 9,9-dioctylfluorene-2,7-diboronic acid and of copolymer have shown a broad peak at 4.5 to 5 ppm, which was not possible to be correctly quantified. Although the presence of that peak indicates boronic OH in the copolymer, we were not able to calculate the copolymer chain length by NMR. The $^1H$ NMR results were coherent with the copolymer formation with the low concentration of the terminal groups.

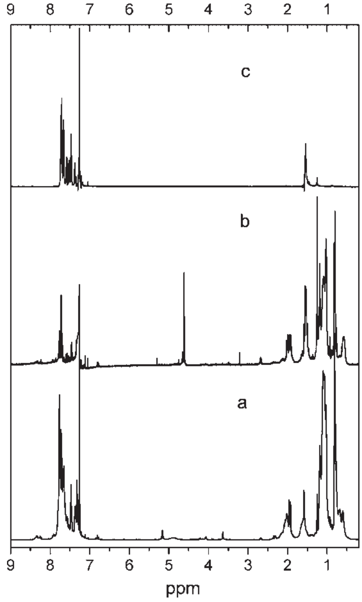

***Figure 2.***
$^1H$ NMR spectra of a) alternating copolymer (1), b) 9,9-dioctylfluorene-2,7-diboronic acid (2) and c)1,4- dibromo-*p*-quaterphenyl (3).

In the copolymer $^{13}C$ NMR spectrum it is possible to observe two distinct C region (aromatic and aliphatic). The 16 aliphatic carbons are distributed in the following peaks: 14, 22.6, 23.7, 23.8, 29.2 (4C), 30 and 31.8 ppm. For the aromatical region, some peaks had been observed between 119.5 and 150 ppm. The C-B bond cannot be clearly observed due to the great number of the aromatic carbons in the copolymer (37). Moreover, the lost of the symmetry due to the boronic group presence made this region more complicate visually. The solution $^{13}C$ NMR spectra of the monomers were not possible to acquire due to their poor solubility. In fact, the $^{13}C$ NMR of 1,4-dibromo-*p*-quaterphenyl was done before in solid state.[12] The spectrum of the pristine material exhibits three resonance peaks at 127, 130, and 137 ppm. The 137 ppm line is attributed to quaternary carbons, the 130 ppm line to outer meta carbons, and the 127 ppm line to all remaining carbons. Furthermore, two other lines at 133 and 132 ppm come from the first and second bromine in the molecules.

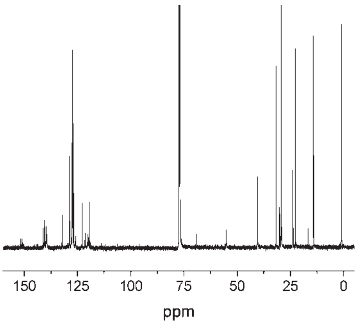

***Figure 3.***
$^{13}C$ NMR of alternating copolymer.

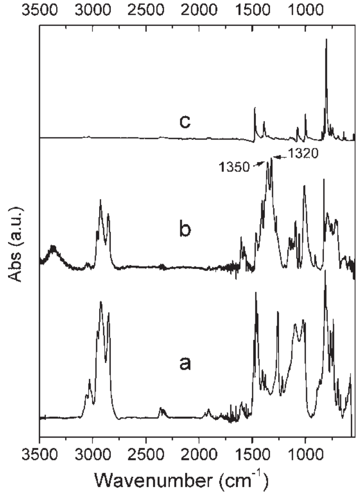

***Figure 4.***
Infrared spectra of a) alternating copolymer (1), b) 9,9-dioctylfluorene-2,7-diboronic acid (2) and c)1,4-dibromo-*p*-quaterphenyl (3).

Figure 4 shows the infrared spectra of monomers (9,9-dioctylfluorene-2,7-diboronic acid and 4,4′-dibromo-*p*-quaterphenyl) and that of the synthesized alternating copolymer. Comparison of these three spectra showing distinct functional group absorptions can be easily analysed in terms of copolymer formation. In spectrum 4 (a), the disappearance of the bands at 1320 and 1350 cm$^{-1}$, characteristics of the B–O bonds in the boronic group in spectrum 4 (b), is an evidence of the formation of the copolymer since boronic groups are removed during the polycondensation reaction. Furthermore, in spectrum 4 (a), both aromatic and aliphatic C–H stretching absorptions are observed at 3029 and 2850–2930 cm$^{-1}$, respectively, along with the aromatic C=C stretching at 1464 cm$^{-1}$ and aromatic C–H out of plane rocking at 814 cm$^{-1}$.

The fact that 30% (mol) of the diboronic acid was used in excess, relative to the other monomer (dibromo), suggests that the alternating block copolymer formed has at the end of the pristine chain a boronic group. However, in the $^1$H NMR and infrared spectra it was not possible to observe it.

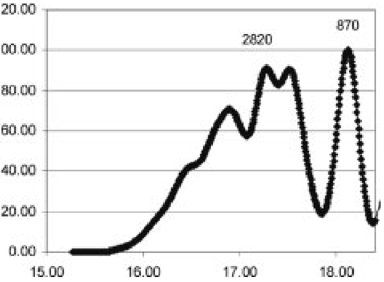

***Figure 5.***
Size exclusion chromatography (SEC) of the block copolymer.

The Suzuki reaction showed to be suited for alternating copolymer formation in good yield (84 %) because of its non-complexity, some product lost is believed to occur during purification due to the good solubility of the product, a low molar mass oligomer having alkylated fluorene, which is desirable for most applications. In this work the relative amount of monomers was set as 2 mol of 4,4′-dibromo-*p*-quaterphenyl to 3 mol of 9,9-dioctylfluorene-2,7-diboronic acid, which may result in a boronic acid - terminated oligomer, presenting a calculated $M_n = 1860\ g \cdot mol^{-1}$. The prepared oligomer will be further reacted to produce a block copolymer bearing electrical charge transport segment, *n* and/or *p* type, along with high PL chromophores, aiming at multifunctional LEDs active layer.

Size exclusion chromatography was performed on different copolymer samples in THF solution. The results compared to calibration with 1,4-dibromo-*p*-quaterphenyl and 9,9-dioctylfluorene-2,7-diboronic acid lead to the conclusion that copolymer samples are composed of a mixture of various oligomer chains, with molar masses ranging from 2500 to 4200 $g \cdot mol^{-1}$, the main peak being centred at 2820 $g \cdot mol^{-1}$. The other peak, centred at 870 $g \cdot mol^{-1}$ reveals short oligomer formation. Assuming a molar mass close to 690 $g \cdot mol^{-1}$ for the constitutive unit *p*-quaterphenyl – dioctylfluorene, a rough calculation gives a degree of polymerisation of 4 units. Additionally, it can be deduced that oligomer lengths goes from 3 to 6 units, a little bit longer than the expected values of 2.5 to 5 units calculated from the reactant molar ratio, according to Carothers equations for stepwise polymerization.

The thermal stability of the copolymer was analyzed by thermogravimetry (TGA) under nitrogen atmosphere (Figure 6). The temperature was increased from 30 to 600 °C at 20 °C/min. The copolymer presented good thermal stability up to a temperature of approximately 300 °C, as good as 4,4′-dibromo-*p*-quaterphenyl and *p*-quaterphenyl. However above this temperature, dibromo *p*-quaterphenyl decomposed continuously up to 440 °C, when 100 % of weight lost was reached. It is interesting to mention that the copolymer presented two decomposition steps and remained stable at a temperature as high as 600 °C, when approximately 50% of its starting weight still remained, compared to the TGA curve of PPP,[13] in which 65% weight lost at 600 °C was observed. These experimental results seem to indicate that the synthesized copolymer is more stable than the monomers and the PPP itself. It was possible to observe by TGA that no weight lost of COP-PPP occurred until 250 °C. Comparatively, PPP, which thermal volatilization initiated at 100 °C has been observed to present at 250 °C a weight lost of 20%.[13]

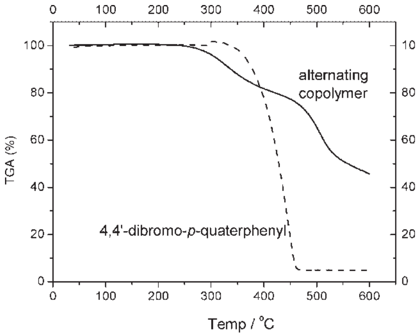

***Figure 6.***
TGA of the 4,4′-dibromo-p-quaterphenyl and the alternating copolymer.

Figure 7 shows the optical absorption and the photoluminescence emission spectra of (a) 9,9-dioctylfluorene-2,7-diboronic acid, (b) 4,4′-dibromo-*p*-quaterphenyl and (c) alternating copolymer in $CHCl_3$. The spectra of the alternating copolymer was also done in solid state (d). In the optical absorption spectrum, a red shift was clearly found for the formed copolymer, with a maximum peaking at 345 nm, whereas it was found at 300 nm for *p*-quaterphenyl and 315 and 290 nm for the diboronic acid. This shift in absorption confirms the formation of the polymer. This result opens up the possibility of tailoring new materials showing an optical absorption different from the starting materials, and shall be helpful to design electroluminescent sensors with higher emissivity and better thermal stability.

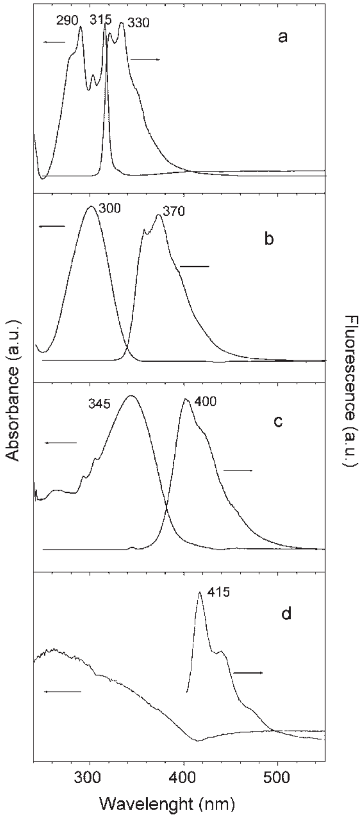

***Figure 7.***
Absorption spectra and Fluorescence emission spectra of (a) 9,9-dioctylfluorene-2,7-diboronic acid, (b) 4,4′-dibromo-*p*-quaterphenyl and (c) alternating copolymer in $CHCl_3$. (d) solid state spectra of the copolymer.

As the light emission process by electroluminescence is the same as by fluorescence - the difference being that the exciton is created by electrical excitation rather than by light irradiation - the measurement of the fluorescence quantum yield allows the evaluation of the role played by fluorescence among the competitive exciton deactivation processes involved. Such an approach allows a rapid screening of the potential chromophores.

In the photoluminescence emission spectrum the maximum appeared to be centered at 400 nm for the copolymer. These spectra show - as in the absorption spectra - a red shift of the copolymer emission as compared to those of the starting monomers. This result agrees well with other experimental results presented above.

Some interesting results concerning the solid state spectra were found. In fact, compared to the liquid one, the optical absorption is not well resolved and no fine structure was observed, however the results in the photoluminescence emission did not correspond. In contrast to the solution spectrum, it is possible to observe in the solid-state spectrum three bands at 415, 440 and 470 nm. The peak maximum at 415 nm is red shifted with respect to that of the solution spectrum (at 400 nm). This effect is usually observed when a solid-state spectrum is compared to a solution spectrum. It may be caused by stronger intermolecular interactions in the solid state.

## Conclusion

The Suzuki reaction was shown suitable to the preparation in good yield of an alternating copolymer from *p*-quaterphenyl and alkyl fluorene with high solubility in chloroform, due to the alkyl substitution at the fluorene 9-position. The reaction also proved to be quite specific and copolymer samples, so far prepared, are comprised by a mixture of oligomers showing polymerization degree close to the calculated values.

The SEC results show a low mass molar of the copolymer, but in the NMR and infrared no evidence of the end group could be seen. The UV-Vis spectroscopy of copolymer has shown absorption and emission spectra red shifted compared to those of the monomers. The copolymer represents a good candidate for some optical applications like light emitting devices and lasers in the blue region.

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[1] N. Miyaura, A. Suzuki, *Chemical Reviews* **1995**, *95*, 2457.
[2] A. Suzuki, in '*Metal-catalyzed Cross-coupling Reactions*', eds. F. Diederich and P. J. Stang, Wiley-VCH, Weinheim, 1998, p. 49.
[3] A. Suzuki, *Journal of Organometallic Chemistry* **1999**, *576*, 147–168.
[4] M. H. Todd, S. Balasubramanian, C. Abell, *Tetrahedron Letters*, **1997**, *38*, 6781.
[5] B. Liu, W.-L. Yu, Y.-H. Lai, W. Huang, *Chemistry of Materials*, **2001**, *13*, 1984.
[6] M. Remmers, B. Mu1ler, K. Martin, H.-J. Ra1der, W. Ko1hler, *Macromolecules*, **1999**, *32*, 1073.
[7] J. Ding, M. Day, G. Robertson, *J. Roovers, Macromolecules*, **2002**, *35*, 3474.
[8] N. Tanigaki, H. Masuda, K. Kaeriyama, *Polymer*, **1997**, *3895*, 1221.
[9] S.-H. Shin, J.-S. Park, J.-W. Park, H. K. Kim, *Synthetic Metals*, **1999**, *102*, 1060.
[10] L. O. Péres, F. Guillet, G. Froyer, *Organic & Biomolecular Chemistry*, **2004**, *2*, 452.
[11] H. W. Furumoto, H. L. Ceccon, *IEEE Journal of Quantum Electronics*, 1970, *6*, 262.
[12] M. Paris, L. O. Péres, O. Chauvet, G. Froyer, *J. Phys. Chem.* B **2006**, *110*, 743.
[13] S. Geetha, D. C. Trivedi, *Synthetic Metals* **2005**, *148*(2), 187.