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Short communication

High yield and stereospecific synthesis of segmented poly (*p*-phenylene vinylene) by the Heck reaction

Carlos Díaz, Diego Alzate, Ricaurte Rodríguez, Cristian Ochoa, Cesar A. Sierra*

Chemistry Department, Universidad Nacional de Colombia, Bogotá, Colombia

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ABSTRACT

A new block copolymer comprised of a 2,5 (p-phenylene vinylene) unit alternating with a hexamethylene unit was synthetized by the Heck methodology using phosphite ligands and two different sources of palladium, with high yields and good polymerization degrees. The spectral characteristics of the polymer are in good agreement with those of its oligomer analogue and its quantum yield (as high as 0.78 vs quinine sulfate as standard) showed to be dependant on the source of palladium employed for the Heck reaction.

1. Introduction

Since the discovery of electroluminescence in polymers by Burroughes et al. [1] research in the field of synthesis and application of macromolecules with extended electronic conjugation has increased considerably, leading in the last 20 years to the development of new materials of actual and future potential application on light emitting diodes, field effect transistors, organic lasers and photovoltaic devices [2–4]. Poly (p-phenylenevinylene) (PPV) derivatives are of particular interest into these macromolecules, mainly because of their chemical versatility and ready synthesis.

A crucial aspect to consider when designing conjugated polymers with optoelectronic properties is to have molecules with a high luminescence quantum yield. In these systems, this property depends on the conjugation length, the nature of the substituents and very important, on the *trans* – pure conformation within the polymer backbone [5]. These light-emitting polymers can be fully or segmented conjugated systems, which rule the extension of the single–double bond conjugation length. The confinement of electronic conjugation, present in segmented copolymers (where rigid conjugated and flexible non-conjugated segments alternate along the polymer backbone) allows to perform theoretical studies of conjugated polymers more easily since the experimental data for the optoelectronic properties comes from a very homogeneous chromophoric system, making possible the correlation of experimental and theoretical data and furthermore improving the solubility and film-forming capability of the polymers [6,7]. Traditionally these polymers have been obtained in high molecular weight by the synthetic methodologies of Wittig and Gilch [8,9]. However, one important disadvantage of these synthetic approaches is the low stereoselectivity to the formation of pure *trans* segments. Therefore, the Heck cross-coupling reaction has arisen as an alternative to solve the aforementioned problem because it guarantees a high stereoselectivity towards *trans* couplings products. Unfortunately, there are plenty of scientific reports that show very low molecular weight polymers obtained with this methodology, which is an enormous drawback for its application [10–12].

With the purpose of improving the suitability of the Heck reaction for the synthesis of PPVs, herein we report the use of triphenyl phosphite as a ligand in the Heck reaction for the synthesis of PPV type polymers and PV type oligomers, based in previous studies carried out in our group, that show a positive effect of triphenyl phosphite ligand in single Heck type couplings with deactivated monomers [13].

2. Experimental

2.1. General considerations

Commercially available precursors were used as received without further purification and solvents were dried according to standard procedures [14]. Inert atmosphere was used for specific reactions (Heck and Wittig). Gel permeation chromatography (GPC) data were obtained using a Waters 2690 in $CHCl_3$ and referenced

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* Corresponding author. Tel.: +57 1 3165000; fax: +57 1 3165220.
E-mail address: casierraa@unal.edu.co (C.A. Sierra).

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against polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained from a Rheometrics STA-625 instrument in nitrogen atmosphere at a heating rate of 10 °C/min. ^{1}H and ^{13}C NMR spectra were taken using a Bruker Avance 400 spectrometer in $CDCl_3$ with TMS as standard. Relative quantum yields (Φ) were measured with a PTI QuantaMaster 40 fluorometer and a Thermo Scientific Evolution 300 UV-vis spectrophotometer, using quinine sulfate in 0.1 M H_2SO_4 as standard ($\Phi = 0.546$), according to a reported procedure [15]. The elemental analysis was taken in a Thermo Scientific Flash 2000 CHNS-O Analyzer, FT-IR spectra were obtained in a Shimadzu IR Prestige-21 FT-IR Spectrophotometer.

2.2. Synthesis of 1,4-diiodo-2,5-dimethoxybenzene (**2**)

This compound was synthesized according to the procedure reported by Zhou et al. [16] with some modifications during the purification: instead of refluxing a chloroform solution of the compound with active carbon, the product was washed several times with an aqueous solution of sodium thiosulfate (10%) in an extraction funnel. From 6.22 g (45.1 mmol) of 1,4-dimethoxybenzene (**1**), 5.46 g (25.5 mmol) of KIO_3 and 12.0 g (47.4 mmol) of I_2 in a solution of 200:2.5:7.5 acetic acid: sulfuric acid: water, 10.2 g of product were obtained as white crystals (58.0%). m.p. 171–173 °C [lit. [16], m.p. 171 °C]. FT-IR (KBr pellet, cm^{-1}): 2954 (w), 2924 (w), 2893 (w), 2831 (w), 1627 (w), 1481 (s), 1442 (m), 1342 (m), 1273 (m), 1211 (s), 1056 (s), 840 (m), 748 (m), 617 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.82 (s, 6H, CH_3), 7.18 (s, 2H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 57.2, 85.5, 121.7, 153.4.

2.3. Synthesis of 3,4,5-trimethoxyethenylbenzene (**4**)

This compound was synthesized according to the procedure reported by Sierra et al. [17] from 11.0 g (55.3 mmol) of 3,4,5-trimethoxybenzaldehyde (**3**), 26.2 g (74.9 mmol) of methyl triphenylphosphonium bromide, 47.0 mL (75.2 mmol) of *n*-butyllithium (1.6 M in hexane) and 120 mL of dry THF, to yield 10.1 g of a yellowish oil (85.3%). FT-IR (liquid, cm^{-1}): 3086 (w), 2958 (s), 2935 (s), 1724 (s), 1692 (m), 1630 (s), 1582 (s), 1505 (s), 1462 (s), 1408 (s), 1326 (s), 1275 (m), 1239 (s), 1184 (m), 1112 (s), 1073 (m), 1007 (m), 943 (w), 838 (m), 777 (m), 744 (w), 707 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.81 (s, 3H, OCH_3), 3.82 (s, 6H, OCH_3), 5.17 (dd, 1H, $J = 10.8$ Hz, $J' = 0.6$ Hz, vinyl-H), 5.62 (dd, 1H, $J = 18$ Hz, $J' = 0.6$ Hz, vinyl-H), 6.58 (dd, 1H, $J = 10.8$ Hz, $J' = 18$ Hz, vinyl-H), 6.59 (s, 2H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.0, 59.7, 103.6, 112.1, 132.1, 135.8, 136.9, 152.2.

2.4. Synthesis of *E,E*-2,5-bis(trimethoxy)-1,4-bis(4-methoxystyryl)benzene (**5**)

In a Schlenk type tube, 81.2 mg (0.208 mmol) of **2**, 70 μL (0.580 mmol) of **4** and 60 mg (0.435 mmol) of potassium carbonate were added together with 2.1 mg (9.4 μmol) of $Pd(OAc)_2$ and 25.0 μL (95.1 μmol) of triphenylphosphite (1 mol% and 10 mol%, respectively). Three consecutive cycles of vacuum/N_2 were applied to the reaction mixture in the Schlenk, and later under positive N_2 pressure, 10 mL of dry DMF were added. The schlenk was closed and the reaction mixture was heated to 120 °C for 48 h. The reaction mixture was filtered in Celite and poured into an acidified HCl (5%) solution, extracted several times with dichloromethane (DCM). The solution was dried, filtered, concentrated under reduced pressure and purified in a chromatography column (silica gel) using hexane–ethyl acetate (10:1). Finally 100.2 mg of a greenish-yellow solid were obtained (92.3%). m.p. 257–259 °C. FT-IR (KBr pellet, cm^{-1}): 3053 (w), 2995 (m), 2937 (m), 1626 (w), 1579 (s), 1508 (s), 1450 (s), 1415 (s), 1350 (m), 1314 (s), 1238 (m), 1184 (s), 1043 (m), 1002 (m), 969 (m), 852 (w), 823 (w), 780 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.90 (s, 6H, OCH_3), 3.96 (s, 18H, OCH_3), 6.80 (s, 4H, phenyl-H), 7.08 (d, 2H, $J = 16.3$ Hz, vinyl-H), 7.15 (s, 2H, phenyl-H), 7.39 (d, 2H, $J = 16.4$ Hz, vinyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.35, 56.52, 61.13, 103.94, 109.38, 122.87, 126.64, 129.26, 133.73, 138.18, 151.65, 153.56. Elemental analysis calculated for $C_{30}H_{34}O_8$: C 68.95, H 6.56, O 24.49. Found: C 69.05, H 6.49, O 23.62.

2.5. Synthesis of 1,6-bis(2,6-dimethoxy-4-vinylphenoxy)hexane (**8**)

This compound was synthesized according to the procedure reported by Sierra et al. [17] in two steps. Starting with the synthesis of the dialdehyde (**7**) from which the target divinyl compound was synthesized through a Wittig reaction. First, a mixture of 4.08 g (22.4 mmol) of 4-hydroxy-3,5-dimethoxybenzaldehyde (**6**) and 2.74 g (11.2 mmol) of 1,6-dibromohexane reacted with 2.70 g (22.6 mmol) of potassium carbonate in 100 mL of dry DMF to yield 4.50 g (45.0%) of a dialdehyde (**7**). Then, the required divinyl product was obtained by continuous stirring of 2.52 g (5.7 mmol) of **7**, 8.07 g (22.6 mmol) of methyltrimethylphosphonium bromide, 15 mL (22.6 mmol) of *n*-buthyllithium (1.6 M in hexanes) in 100 mL of dry THF at room temperature during 12 h, to yield 1.24 g of a white solid (62.0%). m.p. of 42–44 °C. [lit. [18] m.p. no reported] FT-IR (KBr pellet, cm^{-1}): 3078 (w), 2981 (s), 2854 (m), 1581 (s), 1554 (m), 1458 (m), 1411 (m), 1327 (m), 1234 (m), 1110 (s), 987 (w), 894 (w), 825 (w), 709 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.51 (m, 4H, alkyl-H), 1.78 (m, 4H, alkyl-H), 3.85 (s, 12H, OCH_3), 3.97 (t, 4H, $J = 6.7$ Hz benzyl-H), 5.18 (dd, 2H, $J = 10.7$ Hz, $J' = 0.7$ Hz, vinyl-H), 5.59 (dd, 2H, $J = 18$ Hz, $J' = 0.7$ Hz, vinyl-H), 6.59 (dd, 2H, $J = 10.7$ Hz, $J' = 18$ Hz, vinyl-H), 6.62 (s, 4H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 137.5, 136.8, 133.0, 113.0, 103.5, 73.5, 56.1, 30.1, 25.7.

2.6. Synthesis of poly[1,6-hexanedioxy-(2,6-dimethoxy-1,4-phenylene)-1,2-*E*-etenediil-(2,5-dimethoxy-1,4-phenylene)-1,2-*E*-etenediil-(3,5-dimethoxy-1,4-phenylene)] (**9**)

Method 1: Compound **9** was synthesized as **5**, from 0.441 g (1.1 mmol) of **2**, 0.500 g (1.1 mmol) of **8**, 0.401 g (2.9 mmol) of potassium carbonate, 26 μL (0.1 mmol) de triphenylphosphite and 2.2 mg (0.01 mmol) of $Pd(OAc)_2$. The reaction mixture was heated to 120 °C with continuous stirring for about 3 days and then, the reaction mixture was poured in 20 mL of distilled water. The resulting precipitate was filtered off, washed with cold water and dried on vacuum. The catalyst retained in the polymer was eliminated by dissolving the solid in DCM and then passing the solution through Celite. Finally, this solution was concentrated and the polymer was precipitated at 0 °C by dropwise addition of hexane. The solid was filtered again, dried on vacuum and further purification was made by Soxhlet extraction with hexane overnight. Yield 39%, 0.247 g. FT-IR (KBr pellet, cm^{-1}): 2996 (w), 2935 (m), 2862 (w), 2835 (w), 1577 (m), 1501 (s), 1460 (m), 1412 (m), 1320 (m), 1236 (m), 1209 (m), 1112 (s), 1041 (m), 990 (w), 960 (w), 847 (w), 811 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59 (m, alkyl-H), 1.82 (m, alkyl-H), 3.91 (s, OCH_3), 3.94 (s, OCH_3), 4.02 (t, $J = 6.8$ Hz, alkyl-H), 6.77 (s, phenyl-H), 7.05 (d, $J = 16.2$ Hz, vynil-H), 7.12 (s, phenyl-H), 7.35 (d, $J = 16.2$ Hz, vinyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.74, 30.12, 56.22, 56.36, 73.59, 103.91, 109.14, 109.18, 129.18, 144.75, 151.46, 153.65, 155.12, 156.98. Elemental analysis calculated for $C_{34}H_{40}O_8$: C 70.81, H 6.99, O 22.20. Found: C 69.78, H 6.95, O 21.73.

Method 2: The polymerization reaction to obtain compound **9** was done as described in Method 1, but $Pd(dba)_2$ (5.8 mg,