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Effective one-pot synthesis of (*E*)-poly(vinyl arylenes) *via* trans-borylation/Suzuki coupling protocol

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Abstract: A new stereoselective method for the synthesis of (*E*)-poly(vinylarenes) on the basis of the Ru-H catalyzed trans-borylation reaction and sequential Suzuki coupling is described. Two different strategies of Pd-catalyzed polycondensation leading to unsaturated organic macromolecular compounds are discussed. Development of a one-pot procedure reduces costs and time, needed for the separation of intermediates, the amount of organic solvents used for purification and therefore has a positive influence on the process sustainability.

Keywords: one-pot synthesis; organoboron derivatives; poly(arylene vinylene); Suzuki coupling; trans-borylation.

1 Introduction

Modern industry and academia are intensively striving to design and produce new electronic devices which could be applied in solar cells [1, 2], electroluminescence devices [3], novel transistors [4, 5], sensors [6–8] or photovoltaics [9–11]. It is still a challenge to effectively replace silicon-based conducting and optoelectronic materials with their organic, macromolecular counterparts, which are generally cheaper, flexible and easier for preparation. Poly(phenylene vinylenes) (PPVs) are often used as a part (light emitting polymer) of polymer light emitting diodes [12–16]. Organic light emitting diodes and polymer light emitting diodes have become an alternative to traditional light emitters and their role in electronic industry is still increasing [17, 18]. The wide applications of poly(arylene vinylenes) (PAVs) have stimulated the development of new synthetic protocols for the synthesis of these conjugated conducting macromolecular compounds. The most common methods used for the formation of PAVs *via* stoichiometric as well as catalytic reactions are summarized in Figure 1.

Many research groups are engaged in the search for new methods leading to linear and branched PAVs. The conventional stoichiometric approaches providing PAVs include, e.g. the Wittig-Horner polycondensation of α,α′-p-xylenediylbis(triphenylphosphonium chloride) with terephthalaldehyde [19], dehydrogenative Gilch polycondensation of bis(halomethylbenzenes) [20], thermolysis of sulfonium polymer precursors (Wessling route) [21], or Knoevenagel condensation of aldehydes with phenylmethylenes with electron accepting nitrile group in terminal positions [22]. PPVs and other PAVs can be also obtained by chemical vapor deposition using dichloropara[2.2]cyclophane or α,α′-dichloro-*p*-xylene as reagents [23, 24]. High temperature of the process is responsible for a low selectivity towards the products. The problem with halogen removal is the additional drawback of this process, making it useless in the synthesis of PAVs. These stoichiometric methods are often non-selective and lead to the macromolecular compounds with both possible geometries of double C=C bonds, which is undesirable for the final products applications; procedures are often synthetically complicated and demand application of reagents, which are not commercially available.

Synthesis of PAVs is also possible by catalytic methods as acyclic diene metathesis of 1,4-divinylsubstituted arenes [25] or McMurry condensation of dialdehydes or diketones catalyzed by titanium compounds at a low oxidation state [26]. Pd-catalyzed coupling reactions leading to formation of the new carbon-carbon bonds are by far the most popular catalytic methods applied for the synthesis of PAVs. Heck coupling of ethylene or divinylarenes with dihaloarenes leads to PAV with interesting luminescence properties [27–29]. This method was also used for the preparation of copolymer of phenyl vinylene with fluorene, which is a rare example of the polymer emitting red color light [30].

Marciniec et al. [31] described highly effective and selective Hiyama coupling between bissilylethenes and dihaloarenes (mainly dibromoarenes) as the efficient

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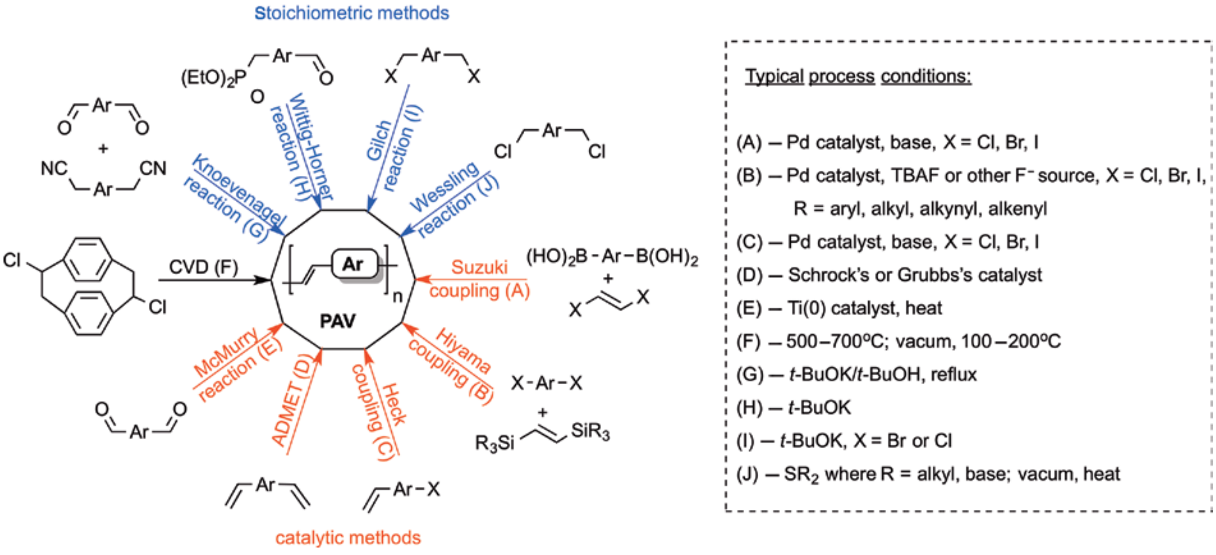


Typical process conditions:

(A) – Pd catalyst, base, X = Cl, Br, I
(B) – Pd catalyst, TBAF or other F^- source, X = Cl, Br, I, R = aryl, alkyl, alkynyl, alkenyl
(C) – Pd catalyst, base, X = Cl, Br, I
(D) – Schrock's or Grubbs's catalyst
(E) – Ti(0) catalyst, heat
(F) – 500–700°C; vacum, 100–200°C
(G) – *t*-BuOK/*t*-BuOH, reflux
(H) – *t*-BuOK
(I) – *t*-BuOK, X = Br or Cl
(J) – SR_2 where R = alkyl, base; vacum, heat

Figure 1: Methods used for the synthesis of poly(arylene vinylene) polymers.

method for the formation of PAVs. The availability of substrates, as well as simplicity of the method, are favorable features of this protocol. Another example of Hiyama coupling leading to the synthesis of (*E*) or (*Z*)-oligo(arylene vinylenes) is the Pd-coupling reaction of 1,4-diiodobenzenes with 1,4-bis(silylethenyl)benzenes [32].

The Suzuki coupling, which is the most commonly used method for the formation of new carbon-carbon bonds, is used also in the formation of PAVs. Oligo(arylene vinylenes) or PAVs obtained according to the Suzuki coupling, due to the retention of the configuration during the reaction, have a high stereoregularity and the type of the reagents determines the formation of macromolecular compounds with *E* or *Z* geometry of the double bond. Wakioka et al. have obtained (*Z*)-PPV by the Suzuki coupling catalyzed by $Pd(PPh_3)_4$ of 2,5-dioctaoxy-1,4-phenyldiboronic acid with (*Z*,*Z*)-bis(2-bromoethenyl)benzene, which was further transformed to (*E*)-PPV by photoisomerization [33].

In this study we would like to report an efficient catalytic method for the synthesis of PPV with *trans* stereoregularity from commercially available reagents: vinylboronates, styrenes and dihaloarenes *via* one-pot strategies based on the trans-borylation (borylative coupling) reaction and Suzuki polycondensation. Two different strategies will be discussed. The first one is based on borylative coupling of vinylboronate with bromosubstituted styrenes and further Suzuki polycondensation of obtained borylethenylbromoarene to PPVs. The homocoupling of vinylboronates followed by the Suzuki coupling with dihaloarenes is the second discussed method. Application of a one-pot procedure has great impact on the processes sustainability, since the separation of the intermediates obtained in trans-borylation reaction is not necessary. Therefore, such a protocol reduces the amount of organic solvents used for the intermediate separation and saves time for their isolation. The whole process is less time-consuming which has a positive influence on its economy.

2 Materials and methods

2.1 Materials

Unless mentioned otherwise, all operations were performed under argon atmosphere (5.0 class, Messer Polska Sp. z o.o., Chorzow, Poland) using the standard Schlenk line technique. Solvents were purified by an mBraun MB SPS 800 purification system and stored over molecular sieves type 4 Å. All dihalogenoarenes, 3-bromostyrene, 4-bormostyrene, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane, $[Pd(PPh_3)_4]$, $[Pd(PCy_3)_2]$, acetone, hexane, THF and toluene were purchased from Sigma-Aldrich, Poznan, Poland. Deuterated solvents were obtained from Dr. Glaser AG Basel, Basel, Switzerland. Potassium carbonate (K_2CO_3), cesium carbonate (Cs_2CO_3), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from P.O.Ch., Gliwice, Poland, Gliwice. Reagents were used as supplied without further purification. Vinylboronates: 2-Vinyl-1,3-dioxaborolane [34] and 2-vinyl-1,3-dioxaborinane [35] were synthesized according to literature methods with some modifications. The ruthenium – $[Ru(CO)Cl(H)(PCy_3)_2$ [36] – and palladium catalyst – $[PdBr(PCy_3)_2Ph]$ [37] $[Pd(dba)(PCy_3)_2]$ [38] were synthesized according to the references.

2.2 Analytical methods

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Varian XL 300 MHz and Varian Gemini 300 MHz spectrometers in chloroform-d_1, benzene-d_6, DMSO-d_6 and THF-d_8 solution. Chemical shifts are reported (in ppm) with reference to the residue solvent. FT-IR spectra were measured on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with a built-in ATR accessory with ATR diamond unit. In all experiments, 16 scans at a resolution of 2 cm^{-1} were used to record the spectra. Gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and thermal conductivity detector (TCD). Mass spectra of the substrates and products were obtained by GC-MS analysis on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. Thermogravimetric (TG) analysis and differential TG analysis (DTG) were carried out using Netzsch TG 209 F1 Libra-Thermo-Microbalance apparatus. All experiments were performed in nitrogen atmosphere at temperatures from the range 30–850°C at the heating rate 10°C/min. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using an Alliance 135 GPCV 2000 apparatus.

2.3 Borylative coupling procedures

The $[\mathrm{Ru(CO)Cl(H)(PCy_3)_2}]$ catalyst (2% mmol) was evacuated in the Schlenk vessel for 20 min, then refilled with argon. Subsequently, toluene, vinylboronate (1.0 mmol) and olefin (1.0 mmol) were added. The concentration of reagents in toluene was approximately 0.5 м. The reaction was carried out for 18 h at 80°C under argon atmosphere. The progress of the reaction was monitored by GC-MS analyses. The solvent was evaporated and the crude product was isolated from the residue of catalyst on silica gel using column chromatography with hexane/ethyl acetate (8/1) as eluent. The product was analyzed on the basis of GC-MS, ^{1}H NMR and ^{13}C NMR. The *E* or *Z* isomer was only formed during the process.

(*E*)-1,2-di(1,3,2-dioxaborinan-2-yl)ethene (1a): Isolated yield: 94%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 1.26 (4H, m, $\mathrm{C}H_2\mathrm{CH_2O}$), 3.42 (8H, br, $\mathrm{OC}H_2$), 6.42 (2H, br, $\mathrm{BC}H\mathrm{=C}H\mathrm{B}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 28.2 ($\mathrm{OCH_2}C\mathrm{H_2CH_2O}$), 68.9 ($\mathrm{O}C\mathrm{H_2CH_2}C\mathrm{H_2O}$) ppm. C_α to boron atom is not observed. MS (EI) (m/z [%]): 196(M$^+$, 23), 138(94), 129(100), 111(7), 67(23), 53(31).

(*E*)-1,2-di(1,3,2-dioxaborolan-2-yl)ethene (1b): Isolated yield: 80%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 3.42 (8H, m, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 6.37 (2H, br, $\mathrm{BC}H\mathrm{=C}H\mathrm{B}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 66.6 ($\mathrm{O}C\mathrm{H_2}C\mathrm{H_2O}$) ppm. C_α to boron atom is not observed. MS (EI) (m/z [%]): 168(M$^+$, 31), 139(87), 111(100), 97(9), 68(41), 53(18).

(*E*)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (1c): Isolated yield: 97%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 1.22 (24H, s, $\mathrm{C}H_3$), 6.54 (2H, br, $\mathrm{B}H\mathrm{C{=}CHB}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 23.7 ($C\mathrm{H_3}$), 84.0 $\mathrm{B(O}C\mathrm{CH_3)}$ ppm. C_α to boron atom is not observed. MS (EI) (m/z [%]): 280(M$^+$, 4), 265(100), 193(20), 152(85), 137(37), 83(95), 55(73).

(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1d): Isolated yield: 92%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 1.11 (12H, s, $\mathrm{C}H_3$), 6.06 (1H, d, $\mathrm{=C}H\mathrm{B}$, $J_{H\text{-}H}$ = 19.1 Hz), 7.00 (1H, d, $\mathrm{=C}H$-Ph, $J_{\mathrm{H\text{-}H}}$ = 18.8 Hz), 7.36–7.42 (2H, $\mathrm{C_6}H_4\mathrm{Br}$), 7.49–7.53 (2H, m, $\mathrm{C_6}H_4\mathrm{Br}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 24.0 ($C\mathrm{H_3}$), 83.4 $\mathrm{B(O}C\mathrm{CH_3)}$, 123.0 128.9, 131.6, 135.4 ($C_6\mathrm{H_4Br}$) 146.7 ($=CH\mathrm{C_6H_4Br}$) ppm. C_α to boron atom is not observed. MS (EI) (m/z [%]): 308(M$^+$, 58), 293(24), 264(11), 251(13), 224(80), 209(7), 143(100), 77(5).

(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e): Isolated yield: 90%; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 1.16 (12H, s, $\mathrm{C}H_3$), 6.11 (1H, d, $\mathrm{=C}H\mathrm{B}$, $J_{H\text{-}H}$ = 19.0 Hz), 6.98 (1H, d, $\mathrm{=C}H$-Ph, $J_{\mathrm{H\text{-}H}}$ = 19.0 Hz), 7.27 (1H, m, $\mathrm{C_6}H_4\mathrm{Br}$), 7.44–7.57 (3H, m,$\mathrm{C_6}H_4\mathrm{Br}$) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$, 25°C): δ = 24.2 ($C\mathrm{H_3}$), 84.1 $\mathrm{B(O}C\mathrm{CH_3)}$, 122.6 127.2, 130.1, 130.9, 131.6. 134.9 ($C_6\mathrm{H_4Br}$) 148.4 ($=CH\mathrm{C_6H_4Br}$) ppm. C_α to boron atom is not observed. MS (EI) (m/z [%]): 308(M$^+$, 4), 293(15), 264(11), 251(9), 223(37), 209(51), 143(100), 77(32).

2.4 Suzuki polycondensation

2.4.1 Homopolycondensation of boryl(boromostyryl)ethenes: A 50 ml Schlenk vessel was charged with $[\mathrm{PdBr(PCy_3)_2Ph}]$ (5% mmol), evacuated for 20 min and refilled with argon. Subsequently (*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 mmol) or (*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 mmol), 2 м aqueous solution of $\mathrm{K_2CO_3}$ (20 mmol) and THF (0.1 м) were added. The reaction was carried out for 24 h at 50°C. The yellow-orange product was filtered, washed with hexane and acetone, dried under vacuum and analyzed by ^{1}H NMR, FT-IR and TG/DTG analysis.

Poly(*p*-phenylene vinylene) (2a): Isolated yield: 86%; ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ = 5.77–6.01 (br, $\mathrm{=C}H$), 6.09–6.33 (br $\mathrm{=C}H$), 7.44–7.63 (br m, Ar) ppm; FT-IR (ATR, cm^{-1}): 783.0, 837.0, 965.6, 1010.4, 1109.0. 1173.2, 1521.2, 1587.2, 1706.2, 2961.4, 3022.0; TG: $\mathrm{t_d}^{5}$ = 160.2, $\mathrm{t_d}^{10}$ = 178.1; char yield: 21.05%.

Poly(*m*-phenylene vinylene) (2b): Isolated yield: 79%; ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ = 5.88 (d, =CH, $J_{H\text{-}H}$ = 15.2 Hz), 6.16 (d =CH, J_{H_H} = 15.4 Hz), 7.39–7.51 (br m, Ar) ppm.; FT-IR (ATR, cm^{-1}): 792.0, 963.8, 1011.2, 1109.2, 1177.0, 1210.0, 1336.0, 1562.0, 2964.0, 3022.9; TG: $\mathrm{t_d}^{5}$ = 235.2, $\mathrm{t_d}^{10}$ = 252.1; char yield: 49.19%.

2.4.2 Polycondensation of bisborylethenes with dihalogenoarenes: A 50 ml Schlenk vessel was charged with $[\mathrm{Pd(Br)(Ph)(PCy_3)_2}]$ (5% mmol), evacuated for 20 min and refilled with argon. Subsequently, bisborylethene (1.0 mmol), dihalogenoarene (1.0 mmol), 2 м aqueous solution of $\mathrm{Cs_2CO_3}$ (20 mmol) and THF (0.1 м) were added. The reaction was carried out for 24 h at 50°C. The product was filtered, washed with hexane and acetone, dried under vacuum and analyzed by ^{1}H NMR, FT-IR and TG/DTG analysis.

Poly(*p*-phenylene vinylene) (3a): Isolated yield: 83%; ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ = 5.96 (d, =CH, $J_{H\text{-}H}$ = 19.1 Hz), 6.12 (d, =CH, $J_{H\text{-}H}$ = 19.1 Hz), 7.31–7.56 (br m, Ar) ppm; FT-IR (ATR, cm^{-1}): 781.0, 835.0, 966.6, 1013.4, 1106.0. 1175.2, 1519.2, 1594.2, 1703.2, 2961.8, 3023.6.; TG: $\mathrm{t_d}^{5}$ = 167.0, $\mathrm{t_d}^{10}$ = 184.7, char yield: 31.03%.

Poly(*m*-phenylene vinylene) (3b): Isolated yield: 74%; ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C): δ = 5.78 (d, =CH, $J_{H\text{-}H}$ = 15.2 Hz), 6.06 (d =CH, $J_{H\text{-}H}$ = 15.4 Hz), 7.30–7.55 (br m, Ar) ppm; FT-IR (ATR, cm^{-1}): 791.0, 965.0, 1009.6, 1111.8, 1179.0, 1215.0, 1332.0, 1565.0, 2968.0, 3024.8; TG: $\mathrm{t_d}^{5}$ = 239.0, $\mathrm{t_d}^{10}$ = 257.5; char yield: 50.28%.

Poly(anthracene-9,10-vinylene) (3c): Isolated yield: 69%; FT-IR (ATR, cm^{-1}): 602.0, 726.0, 906.0, 964.0, 1011.2, 1125.2, 1131.0, 1167.0, 1272.0, 1620.0, 2954.0, 3020.9, 3048.2; TG: $t_d^5=285.2$, $t_d^{10}=341.1$; char yield: 47.05%.

Poly(fluorene-2,7-vinylene) (3d): Isolated yield: 74%; FT-IR (ATR, cm^{-1}): 723.2, 754.0, 820.6, 888.2, 969.0, 1088.2, 1246.8, 1376.4, 1466.2, 1602.0, 2952.2, 3030.0; TG: $t_d^5=240.2$, $t_d^{10}=182.0$; char yield: 44.82%.

Poly(pyridine vinylene) (3e): Isolated yield: 66%; FT-IR (ATR, cm^{-1}): 743.4, 960.0, 1028.2, 1397.4, 1485.2, 1599.0, 1625.8, 2830.4, 3029.0; TG: $t_d^5=260.2$, $t_d^{10}=278.1$; char yield: 36.18%.

Poly(benzophenone-4,4′-vinylene) (3f): Isolated yield: 58%; FT-IR (ATR, cm^{-1}): 699.2, 705.0, 814.0, 966.2, 1020.0, 1076.6, 1177.2, 1206.4, 1281.4, 1690.8, 2966.2, 3018.0; TG: $t_d^5=190.2$, $t_d^{10}=221.1$; char yield: 42.76%.

Poly(2,5-bis(dodecyloxy)-*p*-phenylene vinylene) (3g): Isolated yield: 70%; ^1H NMR (300 MHz, THF-d_8, 25 °C): $\delta=0.91$ (m, CH_3), 1.21–1.42 (m, C_8H_{16}), 3.92 (s, OCH_2) 5.53 (br, =C*H*), 6.74 (br =C*H*), 7.12 (s, Ar) ppm; FT-IR (ATR, cm^{-1}): 722.2, 866.0, 966.2, 865.8, 1041.4, 1218.2, 1391.0, 1420.2, 1470.6, 1504.4, 1607.0, 1677.0, 2204.8, 2852.2, 2925.0, 3033.0 TG: $t_d^5=263.7$, $t_d^{10}=289.5$; char yield: 19.08%.

2.5 One-pot procedure for the synthesis of PAV

2.5.1 Synthesis of PPV *via* trans-borylation of vinylboronate with bromosubstituted styrene and Suzuki coupling: The $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst (2% mmol) was evacuated in the Schlenk vessel for 20 min, then refilled with argon. Subsequently toluene, vinylboronate (1.0 mmol) and bromosubstituted styrene (1.0 mmol) were added. The concentration of reagents in toluene was approximately 0.5 M. The reaction was carried out for 18 h at 80°C under argon atmosphere. The solvent was evaporated and $[PdBr(PCy_3)_2Ph]$ (5% mmol), 2 M aqueous solution of K_2CO_3 (20 mmol) and THF (0.1 M) were added. The reaction was carried out from 5 min to 24 h at 50°C. The product was filtered, washed with hexane and acetone, dried under vacuum to give the corresponding compounds.

2.5.2 Synthesis of PAV *via* homocoupling of vinylboronates and Suzuki coupling: The $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst (2% mmol) was evacuated in the Schlenk vessel for 20 min, then refilled with argon. Subsequently, toluene and vinylboronate (2.0 mmol) were added. The concentration of reagents in toluene was approximately 0.5 M. The reaction was carried out for 18 h at 80°C under argon atmosphere. The solvent was evaporated and the $[PdBr(PCy_3)_2Ph]$ (5% mmol), dihalogenoarene (1.0 mmol), 2 M aqueous solution of Cs_2CO_3 (20 mmol) and THF (0.1 M) were added. The reaction was carried out from 18 h to 24 h at 50°C. The product was filtered, washed with hexane and acetone, dried under vacuum to give the corresponding compounds.

3 Results and discussion

Our general idea was to develop a new, simple, highly effective and stereoselective method for the synthesis of PAVs on the basis of commercially available reagents, taking into account the process time, economy and sustainability. For our studies, we chose two catalytic reactions (trans-borylation and Suzuki coupling), which are characterized with really high selectivity towards specific isomers or give the product with the total retention of the configuration.

Developed by Marciniec, borylative coupling (trans-borylation) of olefins with vinylboronates or their homocoupling yielded the products that can be a source of vinylene fragment for PAVs synthesis in Suzuki polycondensation. The reaction occurs *via* activation of the C-B bond in vinylboronate and the C-H bond in olefin (or the second vinylboronate molecule).

This mode of reactivity seems to be general also for other vinylmetalloids as well as alkynes and reagents with the heteroatom-hydrogen bonds (alcohols, silanols, boronic acids and amines). In the case of the borylative coupling reaction, only *E* isomers are formed in the reaction with olefin. Homocoupling of vinylboronates is less selective, but when 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane is used as a reagent, the *E* isomer is exclusively formed (see Figure 2).

Borylative coupling reactions are catalyzed by ruthenium complexes, which comprise or generate during the process the Ru-H or Ru-B bonds. The most active complex of this transformation is so far $[Ru(CO)Cl(H)(PCy_3)_2]$ (**I**). The process occurred with the evolution of ethylene as a by-product, immediately removed from the reaction system.

Our first strategy for the synthesis of vinylene arylene polymers was based on the formation of monomer for Suzuki polycondensation in the borylative coupling of bromosubstituted styrenes with vinylboronates. The products were obtained with quantitative yield. No homocoupling of vinylboronate was observed, even if an equimolar ratio of reagents was used. The product synthesized within the trans-borylation process was a proper monomer for further polymerization, due to the fact that boron as well as halogen atoms were directly attached to C_{sp^2}, and both required functions were present in the same molecule. Moreover, the exclusive formation of the (*E*) isomer in the borylative coupling reaction has a high impact on the stereoregularity of PAVs, because the Suzuki coupling occurs with the retention of configuration. The trans-borylation was carried out under argon atmosphere at 80°C with 2% mol of catalyst (**I**) in toluene. The conversion of reagents was monitored by GC and GC-MS analyses, while the formation of (*E*) isomer was evidenced by ^1H NMR.

Isolated borylsubstituted bromostyrenes **(1d, 1e)** were tested as monomers in Suzuki polycondensation using

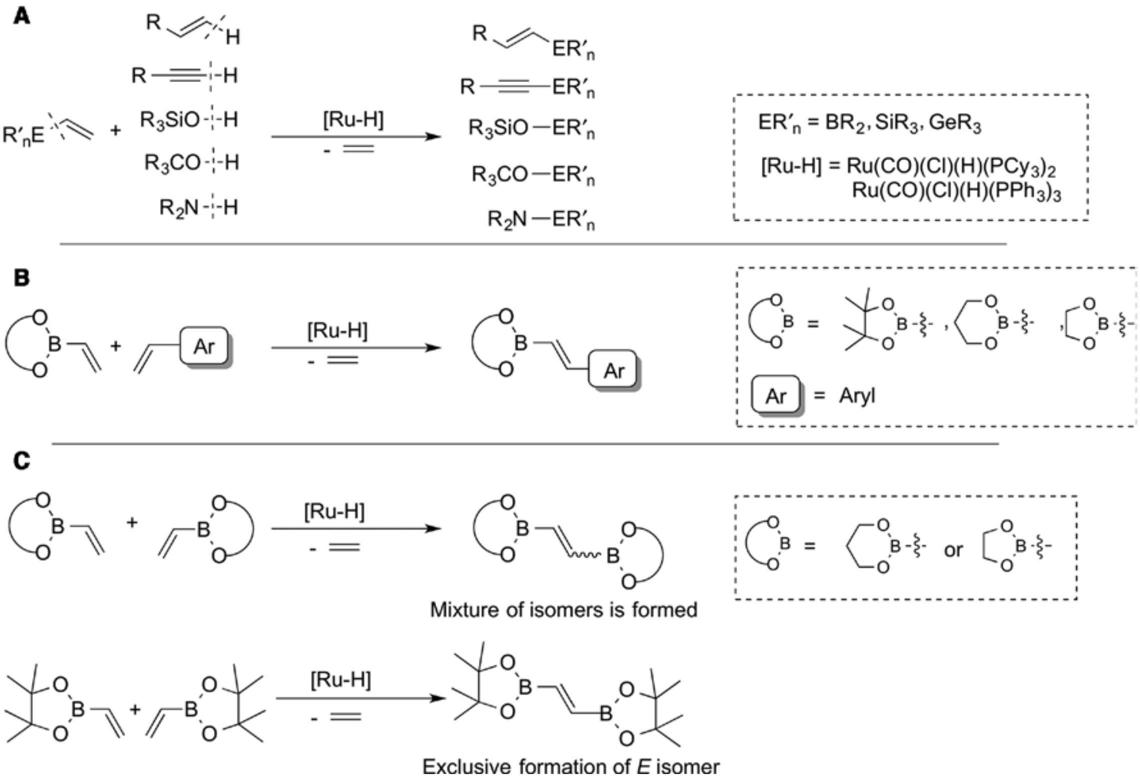


Figure 2: General protocol for: (A) activation of C-H, N-H and O-H bonds by vinylmetalloids, (B) borylative coupling of vinylboronates with olefins, (C) homocoupling of vinylboronates.

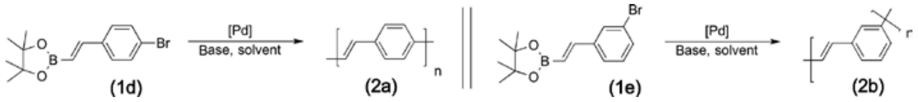
different Pd catalysts, solvents (THF, toluene), reaction temperatures and bases (K_2CO_3, Cs_2CO_3 NaOH, KOH).

We tested several Pd(0) and Pd(II) complexes: $[Pd(PPh_3)_4]$ (**II**), $[PdBr(PCy_3)_2Ph]$ (**III**) $[Pd(PCy_3)_2]$ (**IV**) and $[Pd(dba)(PCy_3)_2]$ (**V**) in the polymerization of both reagents. We used 5 mol% of the catalyst in all procedures. The best results were obtained when the Pd(II) – complex (**III**) was used in the Suzuki coupling. Complete consumption of the reagent was observed after 5 min in the case of borylsubstituted 4-bromostyrene. When borylsubstituted 3-bromostyrene was used as a reagent, its total conversion was observed after 24 h under the same process conditions. The structure of reagents has a surprisingly strong influence on the reaction rate, and when bromine is in the *meta* position to the vinyl substituent, the reaction is much longer. This means that the formation of linear PPVs is much more favorable. The lowest conversion and reaction rates were observer for the most popular catalyst (**II**) used in the Suzuki transformation. Using this Pd(0) complex deborylation, dehalogenation as well as other coupling by-products were observed in the mixture of products. We also checked the influence of the base on the Suzuki coupling for the processes carried out in the presence of catalyst (**II**) and the most active one $[PdBr(PCy_3)_2Ph]$ (**III**). When Cs_2CO_3 and K_2CO_3 were used, comparable results were observed. For 2 M solution of NaOH or KOH, the yields were a bit lower. Because of a lower price of K_2CO_3, relative to that of the cesium analog, its 2 M solution was employed in the reaction procedure. The reaction was much faster in THF then in toluene because of a better solution of the reagents in a more polar tetrahydrofurane. We also noticed the temperature influence on the reagents conversion and the best results were observed when the reaction took place at elevated temperatures. Table 1 presents the optimization of the Suzuki polycondensation for both substrates which differ in the position of bromine atom in the phenyl ring.

On the basis of optimization experiments, the following conditions were chosen for the polycondensation procedure: 5 mol% of catalyst (**III**), 2 M aq. K_2CO_3, THF and 50°C.

Based on the borylative coupling reaction as well as Suzuki polycondensation we proposed a one-pot protocol, which saves time and costs, usually spent for isolation of intermediates. The proposed protocol permits a reduction in the amount of expensive and toxic organic solvents used for separation whereby the whole process has a positive impact on the environment (Figure 3). After

Table 1: Optimization of Suzuki polycondensation procedure for (*E*)-2-(4′-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1d**) and (*E*)-2-(3′-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1e**).



No.	Reagent	[Pd]	Base	Solvent	Temperature (°C)	Time	Conversion/(isol. yield) (%)[b]
1[a]	(1d)	$Pd(PPh_3)_4$	K_2CO_3	THF	50	24 h	37
2			Cs_2CO_3	THF	50	24 h	36
3			KOH	THF	50	24 h	30
4			NaOH	THF	50	24 h	27
5			K_2CO_3	Toluene	50	24 h	32
6			K_2CO_2	THF	80	24 h	55
7		$PdBr(PCy_3)_2Ph$	K_2CO_3	THF	50	5 min	100 (86)
8			Cs_2CO_3	THF	50	5 min	100
9			KOH	THF	50	5 min	87
10			NaOH	THF	50	5 min	83
11			K_2CO_3	THF	20	4 h	100
12			K_2CO_3	Toluene	50	45 min	100
13		$Pd(PCy_3)_2$	K_2CO_3	THF	50	3 h	100
14			K_2CO_3	Toluene	50	3 h	78
15		$Pd(dba)(PCy_3)_2$	K_2CO_3	THF	50	3 h	94
16			K_2CO_3	Toluene	50	3 h	87
17	(1e)	$Pd(PPh_3)_4$	K_2CO_3	THF	50	24 h	27
18		$PdBr(PCy_3)_2Ph$	K_2CO_3	THF	50	24 h	100 (79)
19		$Pd(PCy_3)_2$	K_2CO_3	THF	50	24 h	78
20		$Pd(dba)(PCy_3)_2$	K_2CO_3	THF	50	24 h	75

[a] [Pd]:[(1d) or (1e)]:[base] = $5\times10^{-2}:1:20$, base (2 м) aq. solution.
[b] Determined by GC-MS.

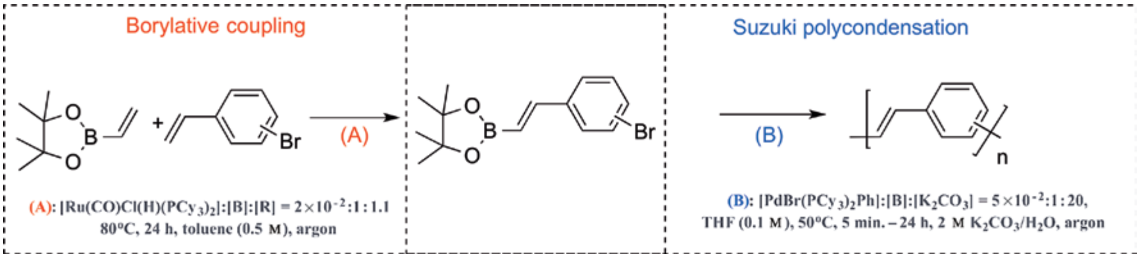


Figure 3: One-pot synthesis of poly(phenylene vinylenes) (PPVs) *via* trans-borylation of vinylboronate with bromosubstituted styrene and Suzuki coupling.

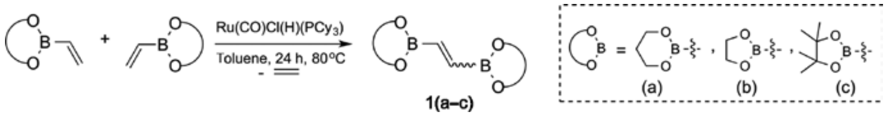
the trans-borylation reaction, THF, the catalyst and K_2CO_3 were added to the vessel and the reaction mixture was heated up to 50°C. The total conversion of reagents, monitored by GC, was observed after a few minutes from the beginning of the process.

The polymer that precipitated during the reaction was filtered off, washed with hexane and acetone to remove low condensed products and the residues of the catalyst and dried under vacuum. The high stereoselectivity as well as linearity of the obtained PPVs polymer are the reasons for the really low solubility of these macromolecular compounds in typical organic solvents. Therefore, their spectroscopic analysis as well as their average molecular weight and polydispersity were difficult to estimate.

The second approach to PAVs, which offers a possibility to incorporate other arenes in the polymer chain, was based on the sequential reaction of vinylboronate homocoupling and Suzuki polycondensation. Homocoupling of vinylboronates leads to bisborylethene, which can be applied as a monomer for the Suzuki polycondensation with dihalogenoarenes.

Table 2 presents the results of homocoupling of different vinylboronates in the presence of catalyst (**I**). For further investigation, bisborylethene obtained from the

Table 2: Influence of vinylboronate on selectivity and productivity of homocoupling reaction.



No.	Vinylboronate	Product	Yield[a] (%)	Selectivity[b] *E*/*Z*
1	(a)	**(1a)**	100	8/1
2	(b)	**(1b)**	88	6/1
3	(c)	**(1c)**	100	1/0

[a]Reaction yields were calculated on the basis of gas chromatographic (GC) analysis.
[b]GC-MS and ^{1}H NMR were used for selectivity determination.

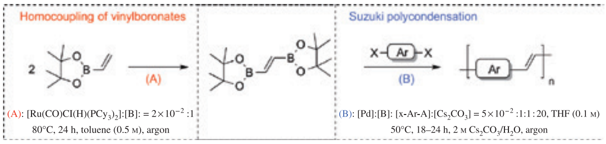
pinacolborane vinyl derivative was chosen, as no (*Z*) isomer was formed in the reaction. A small amount of this undesirable isomer was observed when other vinylbornanes (2-vinyl-1,3,2,-dioxaborolane and 2-vinyl-1,3,2-dioxaborinane) were used as substrates.

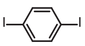
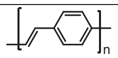
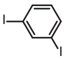
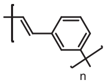
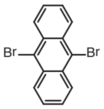
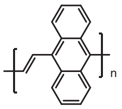
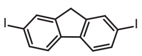
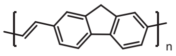
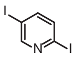
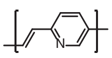
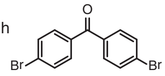
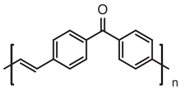
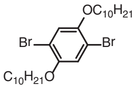
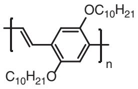
The equimolar ratio of both reagents, bisborylethene and dihalogenoarenes, under the Suzuki polycondensation reaction conditions leads to the formation of macromolecular compounds with vinylene arylene mers. Several dihalogenoarenes, with different functional groups as well heteroatoms in the arene ring, were applied in the polymerization reaction. Two catalysts (**III**) and (**IV**) were used for the polymerization, as their use was the most effective in the first method.

According to the above described one-pot procedure for the synthesis of PPVs, a new protocol of polymerization from commercially available reagents was also developed. Bisborylethene – a homocoupling product was directly used, without any isolation, in the Suzuki polycondensation. After borylative homocoupling of vinylboronic acid pinacol ester, THF, dihalogenoarene, the catalyst and base Cs$_2$CO$_3$ were added and the reaction was carried out for 18–24 h, until the total consumption of reagents, which was monitored by GC analysis (see Table 3). We preliminarily checked that Cs$_2$CO$_3$ gave better results than K$_2$CO$_3$ for the coupling of bisborylethenes with dihalogenoarenes.

The macromolecular compounds precipitated during the polymerization process due to the fact that PAVs are really poorly soluble in traditional organic solvents. The solubility of PAVs is still the main problem for their potential application in electronic industry, which has been tackled by many research groups. Functionalization of the starting reagents with long alkoxy chains slightly improved the solubility of the synthesized polymers, but still was insufficient to calculate their average molecular weight.

Table 3: Synthesis of poly(arylene vinylenes) (PAVs) *via* homocoupling of vinylboranes and Suzuki coupling.



No.	[Pd]	X–Ar–X	Product		Isolated yield (%)
1	PdBr(PCy$_3$)$_2$Ph [III]			**(3a)**	83
2	PdBr(PCy$_3$)$_2$Ph [III]			**(3b)**	74
3	PdBr(PCy$_3$)$_2$Ph [III]			**(3c)**	69
4	Pd(PCy$_3$)$_2$ [IV]			**(3d)**	74
5	Pd(PCy$_3$)$_2$ [IV]			**(3e)**	66
6	PdBr(PCy$_3$)$_2$Ph [III]			**(3f)**	58
7	Pd(PCy$_3$)$_2$ [IV]			**(3g)**	70

The GPC analyses of the obtained polymers were not representative since only the oligomers with short chains (a few mers) were dissolved in THF used for the analysis. Therefore, we are still thinking about another method for polymers analysis. In the near future, we plan to determine the polymer length (the number of mers in the polymer chain) by the elemental analysis of products, and calculate the residue of halogen (bromine or iodide) in the product.

As π-conjugated polymers are really poorly soluble in organic solvents, it was difficult to accomplish their full spectroscopic characterization. The resonance lines characteristic of protons attached to the C=C sp^2 bonds with the coupling constants in the range 15–19 Hz were observed in the ^{1}H NMR spectra recorded mostly in THF-d_8 or DMSO-d_6. Such coupling constants are typical of the compounds with *trans*-stereoregularity. The presence of (*E*)-vinylene functionality was also confirmed by the FT-IR analysis. The CH bending of *trans*-vinylene was visible in all products in the range of 960–969 cm^{-1}, which are characteristic of these groups. The signals assigned to the functional groups attached to arene as well as from heteroarenes were also detected by FT-IR spectroscopy. It is worth emphasizing that Suzuki polycondensation is tolerant to many functional groups attached to arene in monomer and leads to the synthesis of miscellaneous interesting polymers with various electronic and conducting properties. The electronic and electrochemical characteristics of PAVs obtained by the described procedures will be the subject of a separate article in the near future.

The application of arylene vinylene oligomers and polymers in solar and photovoltaic cells, or in optoelectronics, demands determination of their thermal stability because the devices with PAVs work often in high temperatures. The TG analysis and differential thermal analysis were carried out for selected macromolecular compounds (Figure 4). The comparison of thermal properties of PPVs obtained *via* both one-pot procedures did not show any significant difference in their properties. This means that both methods can be interchangeably used for the synthesis of PAVs. The temperatures after which there is 5% or 10% loss in mass are similar for both samples (Figure 4A and B). Increased values of these parameters were observed when alkoxy substituents were attached to the phenyl ring (Figure 4C). Not only the solubility of polymers is slightly better, but also their thermal resistance is higher. TG analyses were carried out for most of the synthesized macromolecular compounds. The properties are in agreement with the literature data.

As follows from a comparison of the one-pot procedures developed within this research with the previously described synthesis of PAVs from bissilylethenes and dihalogenoarenes by Hiyama coupling, the Suzuki polycondensation occurs at a higher rate than the analogous Pd-coupling of silicon compounds. Necessity of the activation of the C-Si bond (increase in the bond nucleophilicity) by TBAF is essential for obtaining high conversion of bissilylethene. This initial step affects the reaction rate. Such an activation is not necessary in the Suzuki coupling and in the applied catalytic condition, the polycondensation occurred immediately.

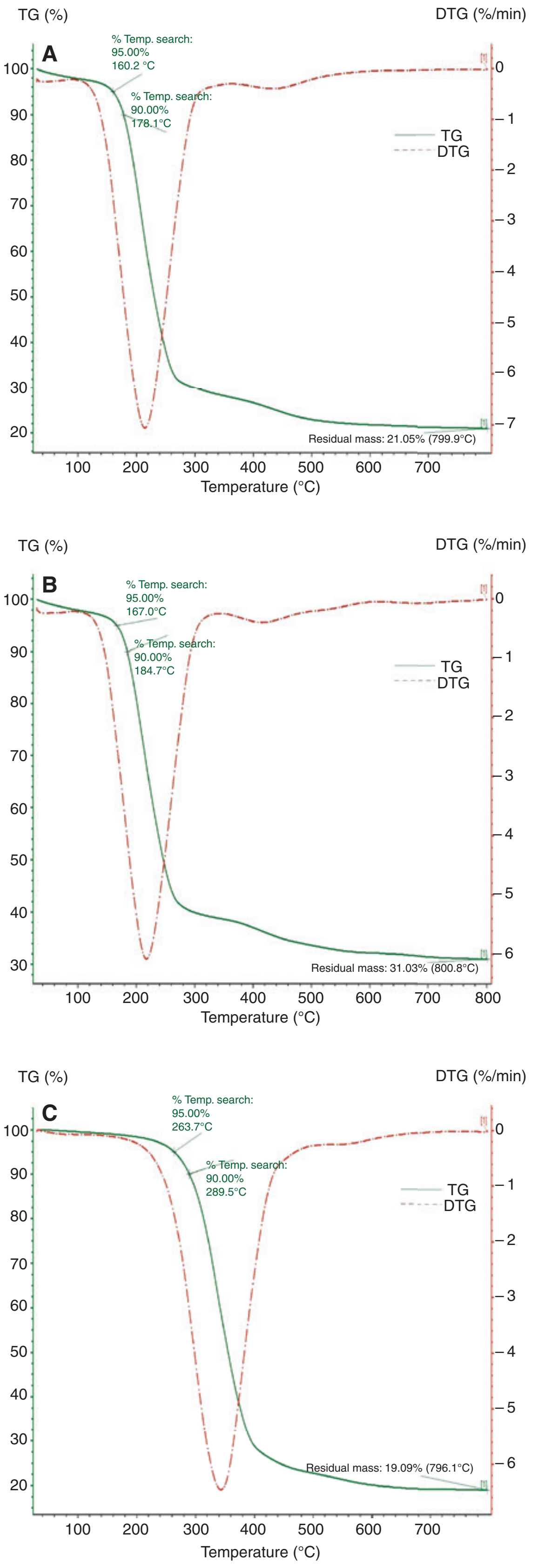


Figure 4: Comparison of thermogravimetric (TG)/differential TG (DTG) analysis of polymers: **2a** (A), **3a** (B) and **3g** (C).

4 Conclusions

Within this study, we developed two highly selective one-pot procedures based on trans-borylation/Suzuki polycondensation for the synthesis of (*E*)-PPVs and (*E*)-PAVs. The first method was based on the borylative coupling of vinylboronates with bromosubstituted styrenes and the polymerization of obtained products *via* Suzuki coupling. Homocoupling of vinylboronates followed by Suzuki polycondensation with dihalogenoarenes are the reactions used in the second synthetic protocol. In both procedures, the reactions occurred at high reaction rates and the products were obtained with high stereoselectivity towards (*E*)-configuration of all double C=C bonds. The use of commercially available reagents, simplicity of the procedures, and their high effectiveness are the main advantages of these methods. Moreover, the reduction in large amounts of organic solvents used for the separation of intermediate trans-borylation products, as well as shortening of the process time and lowering costs of the processes make the process more sustainable and greener. Several PAVs with different arene cores were synthesized according to the developed protocols. Their electronic and electrochemical properties will be a subject of a separate publication.

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References

[1] Yu G, Gao J, Hummelen JC, Wudl F, Heeger AJ. *Science* 1995, 270, 1789–1791.
[2] Chen J, Cao Y. *Acc. Chem. Res.* 2009, 42, 1709–1718.
[3] Grimsdale AC, Leok Chan K, Martin RE, Jokisz PG, Holmes AB. *Chem. Rev.* 2009, 109, 897–1091.
[4] Kano M, Minari T, Tsukagoshi K. *Appl. Phys. Express* 2010, 3, 051601.
[5] Lei T, Xia X, Wang J-Y, Liu C-J, Pei J. *J. Am. Chem. Soc.* 2014, 136, 2135–2141.
[6] Gerard M, Chaubey A, Malhotra B. *Biosens. Bioelectron.* 2002, 17, 345–359.
[7] Guimard NK, Gomez N, Schmidt CE. *Prog. Polym. Sci.* 2007, 32, 876–921.
[8] Janata J, Josowicz M. *Nat. Mater.* 2003, 2, 19–24.
[9] Adam G, Yohannes T, White M, Montaigne A, Ulbricht C, Birckner E, Rathgeber S, Kästner C, Hoppe H, Sariciftci NS. *Macromol. Chem. Phys.* 2014, 215, 1473–1484.
[10] Cheng Y, Yang S, Hsu C. *Chem. Rev.* 2009, 109, 5868–5923.
[11] Marks R, Halls J, Bradley D, Friend R, Holmes A. *J. Phys. Condens. Matter* 1994, 6, 1379–1394.
[12] Burroughes J, Bradley D, Brown A, Marks R, Mackay K, Friend R, Burns P, Holmes A. *Nature* 1990, 347, 539–541.
[13] Chen J-T, Hsu C-S. *Polymer* 2013, 54, 4045–4058.
[14] Rodrigues PC, Fontes BD, Torres B, Sousa WS, Faria GC, Balogh DT, Faria RM, Akcelrud L. *J. Appl. Polym. Sci* 2015, 132, 42579–42586.
[15] Venegoni I, Carniato F, Olivero F, Bisio C, Pira NL, Lambertini VG, Marchese L. *Nanotechnology* 2012, 23, 435702.
[16]] White MS, Kaltenbrunner M, Głowacki ED, Gutnichenko K, Kettlgruber G, Graz I, Aazou S, Ulbricht C, Egbe DA, Miron MC. *Nat. Photon*. 2013, 7, 811–816.
[17] Becker H, Spreitzer H, Kreuder W, Kluge E, Vestweber H, Schenk H, Treacher K. *Synth. Met.* 2001, 122, 105–110.
[18] Zheng H, Zheng Y, Liu N, Ai N, Wang Q, Wu S, Zhou J, Hu D, Yu S, Han S. *Nat. Commun.* 4, 2013, 1–7.
[19] McDonald RN, Campbell TW. *J. Am. Chem. Soc*. 1960, 82, 4669–4671.
[20] Gilch H, Wheelwright W. *J. Polym. Sci. Part A Polym. Chem.* 1966, 4, 1337–1349.
[21] Wessling R, Zimmerman R, Patent 3401152, 19661103, *Chem. Abstr.* 1968, p. 87735.
[22] Lenz RW, Handlovits CE. *J. Org. Chem.* 1960, 25, 813–817.
[23] Iwatsuki S, Kubo M, Kumeuchi T. *Chem. Lett.* 1991, 1071–1074.
[24] Staring E, Braun D, Rikken G, Demandt R, Kessener Y, Bouwmans M, Broer D. *Synth. Met.* 1994, 67, 71–75.
[25] Kumar A, Eichinger B. *Macromol. Rapid Commun.* 1992, 13, 311–314.
[26] Rehahn M, Schlüter AD. *Macromol. Rapid Commun.* 1990, 11, 375–379.
[27] Tsukamoto T, Maeyama K, Higashibayashi S, Sakurai H. *Chem. Lett.* 2015, 44, 1780–1782.
[28] Nojima M, Saito R, Ohta Y, Yokozawa T. *J. Polym. Sci. Part A: Polym. Chem.* 2015, 53, 543–551.
[29] Greiner A, Heitz W. *Macromol. Rapid Commun.* 1988, 9, 581–588.
[30] Zou Y, Pan C, Zhang Z, Liu B, He Y, Zhou K, Zhou Y, Li Y. *J. Cent. South Univ. Technol.* 2010, 17, 269–276.
[31] Prukała W, Pawluć P, Posała K, Marciniec B. *Synlett* 2008, 2008, 41–44.
[32] Katayama H, Nagao M, Ozawa F, Ikegami M, Arai T. *J. Org. Chem.* 2006, 71, 2699–2705.
[33] Wakioka M, Ikegami M, Ozawa F. *Macromolecules* 2010, 43, 6980–6985.
[34] Brinckman F, Stone F. *J. Am. Chem. Soc.* 1960, 82, 6218–6223.
[35] Brown HC, Basavaiah D, Bhat N. *Organometallics* 1983, 2, 1309–1311.
[36] Yi CS, Lee DW, Chen Y. *Organometallics* 1999, 18, 2043–2045.
[37] Barrios-Landeros F, Carrow BP, Hartwig JF. *J. Am. Chem. Soc.* 2009, 131, 8141–8154.
[38] Majchrzak M, Kostera S, Kubicki M, Kownacki I. *Dalton Trans.* 2013, 42, 15535–15539.

Bionotes

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