

# Preparation of alternating $\pi$ -conjugated copolymers involving electrochemically generated aryldizinc intermediates

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We describe in this paper an original synthetic route to alternating  $\pi$ -conjugated copolymers, based on the electrochemical preparation of intermediate aryldizinc species and their subsequent coupling with unsaturated dihalogenated compounds. This method was first applied to the preparation of poly(*p*-phenylenevinylene)s (PPVs). The structural and redox properties of PPVs prepared in this way are discussed. Some copolymers exhibiting alternating phenyl and thienyl units are also prepared according to this procedure.

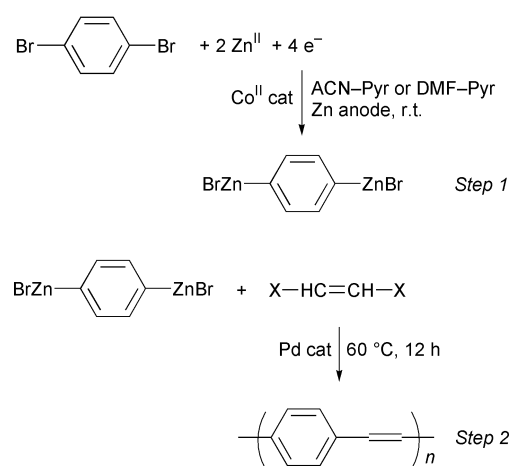
The preparation of  $\pi$ -conjugated polymers has received much attention in the past two decades since these organic materials emerged as very promising materials for electronic or optoelectronic devices.<sup>1</sup> In this context, poly(*p*-phenylenevinylene)s (PPVs) have been intensively explored owing to their electroluminescent properties.<sup>2,3</sup> One of the most versatile synthetic routes to these materials involves the intermediate formation of sulfonium salts, followed by hydrolysis, dialysis and elimination steps.<sup>4</sup> Some other strategies use Knoevenagel<sup>5</sup> polycondensation for the preparation of substituted PPVs. Yamamoto and coworkers have developed an organometallic procedure affording the synthesis of PPV-like polymers with repeating phenyl-vinyl-phenyl units.<sup>6</sup> As a matter of fact, organometallic routes have been developed more specifically for the preparation of regioregular poly(3-alkylthiophenes) by the groups of Rieke,<sup>7</sup> Mc Cullough<sup>8</sup> and Bidan<sup>9</sup> since these methods provide an enhanced conjugation length, improving the electronic properties of these materials. We have recently achieved the cobalt-catalyzed electrochemical preparation of aryldizinc compounds from the corresponding aryl dihalides.<sup>10</sup> The activation by zinc of two positions of aromatic rings could allow the preparation of alternating copolymers by coupling with another organic dihalide.

In this work, we present a two-step preparation of alternating  $\pi$ -conjugated copolymers based on the electrochemical preparation of the above-mentioned aryldizinc intermediates. The second step is a palladium-catalyzed coupling of the latter zinc species with vinyl or aryl dihalides. We first focused on the preparation of PPVs according to the overall process represented in Scheme 1. The structural and redox properties of the resulting polymers are discussed, as well as the effect of substitution on the phenyl ring. Lastly, this method has been extended to the preparation of some alternating phenyl and/or thienyl copolymers.

## Experimental

### Reagents

*N,N*-Dimethylformamide (DMF) and acetonitrile used as solvents were purchased from SDS (analytical grade) and used without further purification. Substrates (1,4-dibromobenzene and its substituted derivatives, 3-substituted-2,5-dihalo-



Scheme 1

phenes, 1,2-dibromoethylene) were purchased from Aldrich and Acros chemicals and used without further purification. (*E*)-1,2-dichloroethylene was obtained from Lancaster. Tetra-butylammonium tetrafluoroborate was purchased from Fluka and recrystallized in diethyl ether.  $\text{CoCl}_2$  catalyst precursor was purchased from Acros and stored in a dry atmosphere.  $\text{PdCl}_2(\text{PPh}_3)_2$  catalyst was purchased from Aldrich.

### Protocol of reactions

The electrochemical preparation of aryldizinc species was achieved from 10 mmol of the starting 1,4-dibromophenylene in 95 : 5 DMF–pyridine or acetonitrile–pyridine mixtures in an undivided cell fitted with a sacrificial zinc anode. The conditions used in this first electrochemical step are fully described in ref. 10. The Pd-catalyzed Negishi polymerization of the resulting aryldizinc species was carried out in the same medium by adding an equimolar amount (10 mmol) of the 1,2-dihaloethylene and 280 mg (0.4 mmol) of  $\text{PdCl}_2(\text{PPh}_3)_2$ . The solution was stirred and heated (60 °C) for 12 h.

After polymerization, the solutions were poured into aqueous 6 N HCl solutions. The resulting precipitate was filtered and washed with the same solution, then several times with distilled water, methanol and pentane in order to remove

low-mass oligomers. For unsubstituted poly(*p*-phenylenevinylene), the solid residue was purified on a Soxhlet extractor with the same solutions. Finally, the polymers were dissolved in chloroform and re-precipitated in methanol, and dried under vacuum for 12 h.

## Apparatus

Electrolyses were carried out using an HP E3611 A DC power supply at a constant current of 0.25 A in all experiments. Cyclic voltammograms were recorded using an EG&G-PARC 273 A potentiostat and the M270 electrochemical software. The concentration of the nonpolymeric substrates was monitored by GC using an internal standard (dodecane or tetradecane) from aliquots of the solutions, which were iodolyzed in order to give the iodinated equivalents of the arylzinc species. <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AC 200 spectrometer. IR spectra were recorded on a Perkin Elmer 577 FTIR Spectrophotometer from KBr pellets. UV-visible spectra were recorded on a Cary 50 spectrophotometer from the chloroform-soluble fractions of the polymers. MALDI-TOF-MS spectra were realised at the Laboratoire de Chimie Structurale Organique et Biologique (LCSOB, Université Pierre et Marie Curie, Paris) using dithranol as the matrix and either AgTFA or NaI as cationization salts.

## Polymer characterization

The polymers prepared have been characterized by several techniques, namely IR spectrophotometry, MALDI-TOF-MS, <sup>1</sup>H-NMR, and cyclic voltammetry. Size exclusion chromatography did not give satisfactory results using polystyrene calibration standards, since the molecular weights determined were considerably overestimated compared to the fragments observed in the MALDI spectra.

**Poly(*p*-phenylenevinylene).** Pale brown powder, partially soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.5$  V/SCE and reduction potential:  $E = -1.8$  V/SCE. UV-Visible (CHCl<sub>3</sub> soluble fraction):  $\lambda_{\text{max}} = 367$  nm. IR (KBr pellet): 1599; 1485; 1413 ( $\delta$  C=C) cm<sup>-1</sup>.

**Poly[(2-methyl-1,4-phenylene)vinylene].** Brown powder, soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.6$  V/SCE and reduction potential:  $E = -2.0$  V/SCE. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.40–7.20 (m); 2–1.6 (m). UV-Visible (CHCl<sub>3</sub> soluble fraction):  $\lambda_{\text{max}} = 355$  nm.

**Poly[(2,5-dimethyl-1,4-phenylene)vinylene].** Brown powder, soluble in CHCl<sub>3</sub>. IR (KBr pellet): 1641; 1500; 1437 ( $\delta$  C=C); 808 ( $\delta$  C<sub>sp<sup>2</sup></sub>-H) cm<sup>-1</sup>.

**Poly[(2-fluoro-1,4-phenylene)vinylene].** Brown powder, soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.7$  V /SCE and reduction potential:  $E = -1.7$  V/SCE.

**Poly(1,4-phenylene-co-2-nitro-1,4-phenylene).** Black powder, soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.9$  V/SCE and reduction potential:  $E = -1.4$  V/SCE. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.90–7.10 (m). IR (KBr pellet): 1640; 1529; 1468 ( $\delta$  C=C); 1352 ( $\nu$  NO<sub>2</sub>) cm<sup>-1</sup>.

**Poly(1,4-phenylene-co-3-methyl-2,5-thienylene).** Brown powder, partially soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.6$  V/SCE. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.53–6.96 (m); 2.30–2.10 (m). UV-Visible (CHCl<sub>3</sub> soluble fraction):  $\lambda_{\text{max}} = 387$  nm.

**Poly(2-methyl-1,4-phenylene-co-2,5-thienylene).** Brown powder, partially soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.2$

V/SCE. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.43–7.0 (m); 2.45–2.30 (m). UV-Visible (CHCl<sub>3</sub> soluble fraction):  $\lambda_{\text{max}} = 360$  nm.

**Poly(1,4-phenylene-co-3-acetyl-2,5-thienylene).** Brown oil, soluble in CHCl<sub>3</sub>. Oxidation potential:  $E = 1.5$  V/SCE and reduction potential:  $E = -1.7$  V/SCE. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  8–7.2 (m); 2–1.6 (m).

## Results and discussion

### Preparation of unsubstituted PPV

Step 1 is carried out in an undivided cell fitted with a sacrificial zinc anode (acting as Zn<sup>II</sup> cation source). The electrolysis is carried out at a constant current of 0.25 A until total consumption of the original 1,4-dibromobenzene. For all electrolyses, 1,4-dibromophenylenes are consumed according to the expected faradaic slope, that is 4 Faraday per mole of substrate. Further details concerning the electrolyses, namely the evolution of the product distribution, is described in ref. 10.

Step 2 is achieved in the same cell, immediately after the electrolysis. An equimolar amount (10 mmol) of 1,2-dihaloethylene is added to the solution, together with 2 mol % of Pd catalyst. The solution is heated at 60 °C for 12 h. After this time, both the arylzinc species and 1,2-dihaloethylene are consumed, which was verified by GC. This Pd-catalyzed Negishi coupling was carried out from either a mixture of (*Z*)- and (*E*)-1,2-dibromoethylene, or from pure (*E*)-1,2-dichloroethylene. The latter substrate was used in order to incorporate only “*trans*” vinyl units within the polymer. The isolated yields obtained are reported in Table 1. These yields are in the 25 to 55% range, depending on the vinyl dihalide introduced and on the medium used. Since the arylzinc species are formed in good yields (50–70%),<sup>10</sup> the values reported in Table 1 are most likely affected by losses during the purification steps.

### Characterization of PPV

**<sup>1</sup>H-NMR.** The PPV were first characterized by <sup>1</sup>H-NMR of the chloroform-soluble fraction collected after purification. The spectra corresponding to the aromatic region are reported in Fig. 1 for PPV prepared from the (*Z*)- and (*E*)-1,2-dibromoethylene mixture, and from (*E*)-1,2-dichloroethylene.

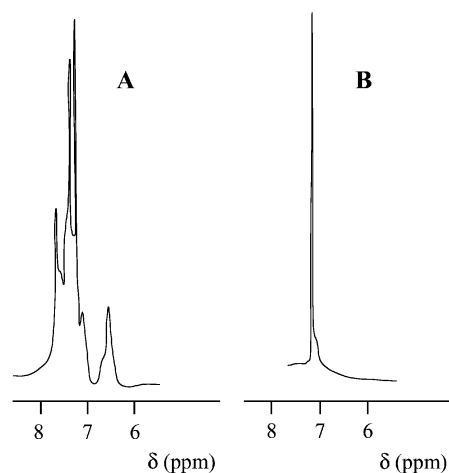
The general shape of these spectra are close to those corresponding to stilbene. As a matter of fact, the spectrum of PPV prepared from the mixture of stereoisomers exhibits two broad signals between 6 and 8 ppm analogous to the spectrum of *cis* + *trans* stilbene mixtures. Conversely, the spectrum of PPV prepared from (*E*)-1,2-dichloroethylene shows a unique signal above 7 ppm. So the original configuration of the vinyl substrates seems to be retained within the polymer structure.

**MALDI-TOF MS.** The MALDI spectra of the same polymers are presented in Fig. 2. In both spectra, peaks are

**Table 1** Two-step preparation of PPV

Medium	Isolated yield (%) <sup>a</sup> for PPV prepared from	
	( <i>Z</i> + <i>E</i> )-Br-CH=CH-Br	( <i>E</i> )-Cl-CH=CH-Cl
CH <sub>3</sub> CN-pyr	40–55 <sup>b</sup>	25
DMF-pyr	—	33

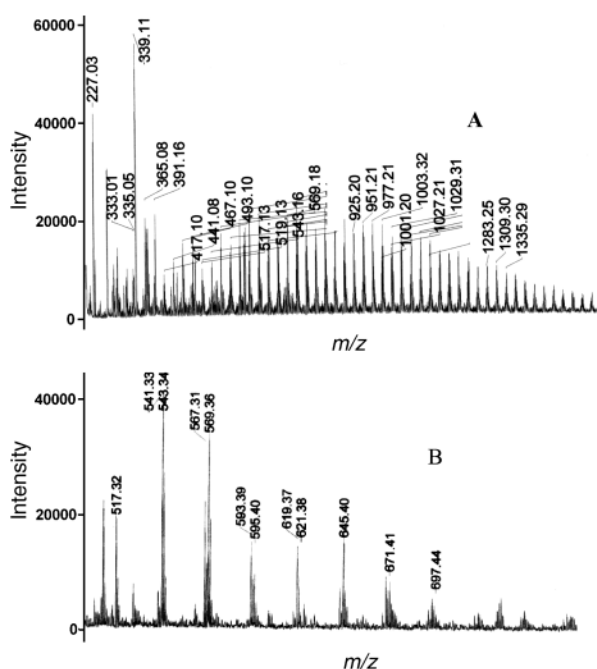
<sup>a</sup> Yields calculated from the mass of solid recovered *vs.* that of the starting dibromobenzene, neglecting the mass of possible halogen end groups. <sup>b</sup> Range determined from several experiments.



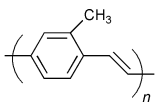
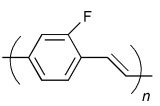
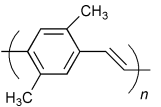
**Fig. 1**  $^1\text{H}$ -NMR spectra ( $\text{CDCl}_3$ , ref. TMS) of the chloroform-soluble fraction of PPV prepared from a mixture of (*Z* + *E*)-1,2-dibromoethylene (**A**) and pure (*E*)-1,2-dichloroethylene (**B**).

separated by 102  $m/z$  mass units, corresponding to the monomeric unit of PPV. Some peaks exhibit a difference of  $\pm 80$  ascribed to the presence of brominated end groups. PPV prepared from the mixture of (*Z*)- and (*E*)-1,2-dibromoethylene shows higher mass fragments, which could explain the higher yields obtained from this vinyl dibromide since high molecular weight fragments are less soluble in most solvents and therefore more quantitatively extracted. Moreover, UV-visible spectra recorded for both polymers exhibit maxima at respectively  $\lambda_{\text{max}} = 367$  nm for PPV containing *cis* + *trans* vinyl moieties and  $\lambda_{\text{max}} = 327$  nm for its pure *trans* analogue, revealing a higher conjugation length for the first polymer.

Size exclusion chromatography has been performed for the polymer prepared from the mixture of *cis* + *trans* vinyl dihalide (referred to as **A** in Figs. 1 and 2). As already mentioned in the experimental section, the calibration carried out from polystyrene standards is not adapted to the determination of the molecular weight of rigid  $\pi$ -conjugated polymers such as PPV. The average molecular weight of the chloroform-soluble

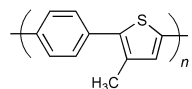
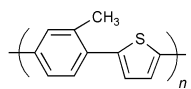
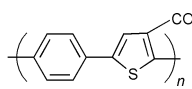
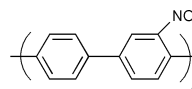


**Table 2** Two-step preparation of substituted PPVs

Polymer			
Isolated yield (%) <sup>a</sup>	78	20	15
Redox doping processes/V vs. SCE	$E_p = 1.6$ $E_n = -1.95$	$E_p = 1.7$ $E_n = -1.7$	Not observed

<sup>a</sup> Yields calculated from the mass of solid recovered vs. that of the original substituted dibromophenylene, neglecting the mass of possible halogen end groups.

**Table 3** Preparation of various copolymers in DMF. The aryldizinc intermediate is always prepared from the aromatic ring represented on the left

Polymer				
Isolated yield (%) <sup>a</sup>	54	64	16	90 <sup>b</sup>
Redox doping processes/V vs. SCE	$E_p = 1.6$	$E_p = 1.2$	$E_p = 1.5$ $E_n = -1.7$	$E_p = 1.9$ $E_n = -1.4$

<sup>a</sup> Yields calculated from the mass of solid recovered vs. that of the starting substituted dibromobenzene, neglecting the mass of possible halogen end groups. <sup>b</sup> Obtained after 48 h of the Pd-catalyzed coupling reaction with 2,5-dibromonitrobenzene at 90 °C in DMF.

dibromobenzene. The redox properties of the resulting PPVs have been studied, and both mono-substituted polymers exhibit p- and n-doping processes. Dimethyl-substituted PPV was found to be too insulating in our conditions and therefore neither oxidation nor reduction processes were observed on the voltammograms.

### Other $\pi$ -conjugated copolymers

We have undertaken to extend the procedure reported above to the preparation of copolymers exhibiting alternating aryl or heteroaryl moieties. The formation of the original aryldizinc species has been achieved in DMF in the same conditions as above reported. The second palladium catalyzed coupling step (60 °C for 12 h, unless otherwise stated) has been carried out either from 1,4-dihaloobenzenes or from 2,5-dihalothiophenes. The results are summarized in Table 3.

The yields are moderate to excellent. The alternating benzene/nitrobenzene polymer has been obtained at higher temperatures and for a longer reaction time. Our method shows a good functional group compatibility, as acetyl and nitro groups are retained in the polymer structure. The oxidation and/or reduction processes of these materials are consistent with both their expected structure and the electronic effects of their substituents. Such a synthetic strategy might be of interest for the preparation of materials bearing alternating donor/acceptor units.

### Conclusion

The electrochemical preparation of aryldizinc species allows their subsequent copolymerization with 1,2-dihaloethylene under Negishi conditions using catalytic amounts of palladium catalyst. Unsubstituted PPV is obtained in moderate to good yields, depending on both intermediate aryldizinc formation and on the losses met along the purification steps. PPVs obtained by this procedure show structural differences when prepared from different vinyl stereoisomers, suggesting that

the original configuration of the vinyl moiety is retained. The structure of PPV has been confirmed both by MALDI-MS and by cyclic voltammetry. The presence of substituents on the phenyl ring affects the formation of the organozinc intermediates and therefore the polymer yields. Some phenyl/thienyl and phenyl/phenyl copolymers have also been prepared with a good functional compatibility, underlining the versatility of the method.

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