PERKIN 1 COMMUNICATION

Heck reaction of bis-arenediazonium salts with vinyltriethoxysilane: a new synthetic protocol for poly(1,4-arylenevinylene)s †

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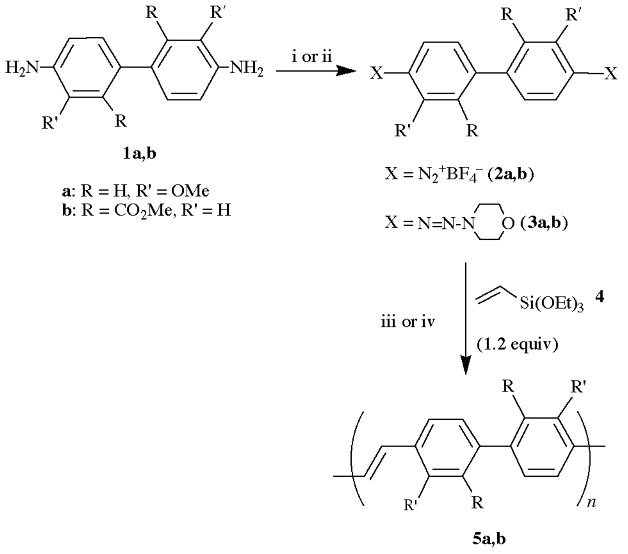
A new synthetic protocol for poly(1,4-arylenevinylene)s *via* the first-ever poly-Heck reaction of arenediazonium salts with vinyltriethoxysilane is described.

The discovery that poly(1,4-phenylenevinylene)s (PPVs) have outstanding optoelectronic properties and can be effectively used as emission layers in light-emitting diodes (LEDs)[1] has stimulated widespread activity in the synthesis of such rigid-rod polymers.[1–3] Poly(phenylenevinylene)s are classically prepared *via* elimination from sulfonium salt polymer precursors, dehydrohalogenation of xylylene dihalides and Wittig or McMurry condensation reactions.[1] However, these methods usually require harsh reaction conditions and hence are not suitable for the synthesis of functionalized PPVs, especially for the organic soluble variants having lateral substituents. In 1988, Greiner and Heitz reported an alternative synthetic route to PPVs *via* Heck reaction of aromatic dibromides with ethylene.[4] Since then, this poly-Heck reaction strategy, by virtue of its mild reaction conditions and high functional group tolerance properties, has evolved as a superior methodology for the synthesis of poly(phenylenevinylene)s.[2,3] We have recently shown that arenediazonium salts have several advantages over aryl halides in Heck reactions : mild and operationally simple reaction conditions (ligandless Pd-catalyst, no added base, room temperature to 80 °C), short reaction times (15 min to 1 h) and most significantly, an enhanced reactivity over aryl bromides and even the iodides.[5] In view of these and the fact that a wide variety of anilines and bis-anilines are more readily available than aryl halides, poly-Heck reaction of bis-arenediazonium salts promised to be an attractive alternative for the synthesis of poly(phenylenevinylene)s. In a model reaction, we have described the double Heck-reaction of monoarenediazonium salts with vinyltriethoxysilane, an inexpensive and easily handled ethylene-equivalent,[6] for the synthesis of symmetrical *trans*-stilbenes in high yields.[7] Based on these results, we now present the first ever poly-Heck reaction using bis-arenediazonium salts and vinyltriethoxysilane towards a facile new synthesis of poly(arylenevinylene)s with high degrees of regioselectivity.

Table 1 Physical properties of the polymers **5a**,**b**[a]

	UV λ_{max}	PL λ_{max}	M_w[b]	M_n[b]	M_w/M_n
5a	390 nm	465 nm	33118	31010	1.06
5b	338 nm	430 nm	11748	10834	1.08

[a] THF soluble fractions; [b] polystyrene standard.



Scheme 1 *Reagents and conditions*: i) NaNO$_2$, dil. HCl, 0 °C, NaBF$_4$; ii) NaNO$_2$, dil. HCl, 0 °C, morpholine, NaHCO$_3$; iii) for **2a**,**b**: 10% Pd(OAc)$_2$, EtOH, 80; iv) for **3a**,**b**: 70% HClO$_4$ (4 equiv.), 10% Pd(AOc)$_2$, EtOH, 80 °C.

In the event, the readily available benzidine derivatives **1a**,**b** were converted to the corresponding bis(diazonium tetrafluoroborate)s **2a**,**b** and the latter reacted with vinyltriethoxysilane (**4**) (1 equiv.) in the presence of 5–10% Pd(OAc)$_2$ in refluxing EtOH–CH$_2$Cl$_2$ to give the polymers **5a**,**b** (Scheme 1). In these reactions, the bis-triazenes **3a**,**b** could also be used as the bis-diazonium salt surrogates.[8] Thus, poly-Heck reaction **3a**,**b** with **4** (1 equiv.), under identical reaction conditions but having 4 equiv. of 70% HClO$_4$ to liberate the bis(diazonium) salts **2a**,**b** *in situ*, produced the polymers **5a**,**b** with equal efficacy. The polymers were purified through filtration, Soxhlet extraction with CHCl$_3$ and reprecipitation with MeOH. Despite lacking large lateral substituents, but perhaps due to the presence of the twisted biphenylene units, these polymers were found to be appreciably soluble in CHCl$_3$ and partly in THF to enable their physical characterization (Table 1). The UV and PL-maxima of these polymers, as compared to poly(phenylenevinylene)s, expectedly underwent a hypsochromic shift. Between **5a** and **b**, the latter showed a lower absorption maximum as a result of the more twisted nature of its *ortho*,*ortho*′-disubstituted biphenylene unit. GPC measurements on **5a**,**b** against a polystyrene standard gave average moleculer weights of *ca.* 33 000 and 11 000, respectively, with excellent M$_w$/M$_n$ ratios (~1) which compares favorably with those obtained for PPVs prepared *via* poly-Heck reactions of aromatic dibromides with ethylene.[4] The lower molecular weight distribution observed for **5b** is perhaps due to the electron-deficient nature of the bis-diazonium salt **2b** which favors a SET-induced dediazoniation pathway leading to premature chain termination. The high regioselectivity of this poly-Heck reaction is evident from the ^{1}H and ^{13}C NMR spectra of these polymers which showed ≤10% contamination from 1,1-diarylenevinylene units present in the chain.‡ It may be noted that poly-Heck reactions of aromatic dibromides and ditriflates with ethylene reportedly produce up to 20% of the 1,1-disubstituted contaminants.[9] Such structural defects result in interrupted conjugation in the polymer chain and may profoundly influence the optical properties of the

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† ^{13}C and ^{1}H NMR spectra of **5a** and **5b** are available as supplementary data available from BLDSC (SUPPL. NO. 57600, pp. 4) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

polymer. The higher regioselectivity obtained in poly-Heck reactions using bis-arenediazonium salts thus provides a significant methodological improvement in PPV synthesis. However, the exact reasons for such high regioselectivity are not clear to us at this moment but may be attributed to the cationic aryl-Pd species[10,11] that are presumably involved in these reactions.

In summary, we have described the first ever poly-Heck reaction of arenediazonium salts for the synthesis of poly(arylenevinylene)s. The attractive features of this protocol are: ready availability of starting materials, mild reaction conditions, high regioselectivity and the strategic use of vinyltriethoxysilane as a cheap, easily handled ethylene equivalent. Since we and others have recently shown that arenediazonium salts can be efficiently cross-coupled with aryl boronic acids,[12] synthesis of poly(1,4-phenylene)s *via* poly-Suzuki coupling of bis-arenediazonium salts is an equally promising prospect that is under current investigation.

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Notes and references

‡ Vinyl protons of 1,1-diarylethylenes appear at 5.0–5.3 ppm whereas those of the 1,2-isomers appear at 6.8–7.0 ppm.

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