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A new approach to the synthesis of substituted bithiophene and polymers containing thiophene

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Abstract—Palladium-catalyzed reaction of $Bu_3SnSnBu_3$ with bromo-substituted thiophene or bromo-substituted thiophene-containing monomers is found to generate bithiophene or symmetric polymers containing thiophene in very good yields, respectively.

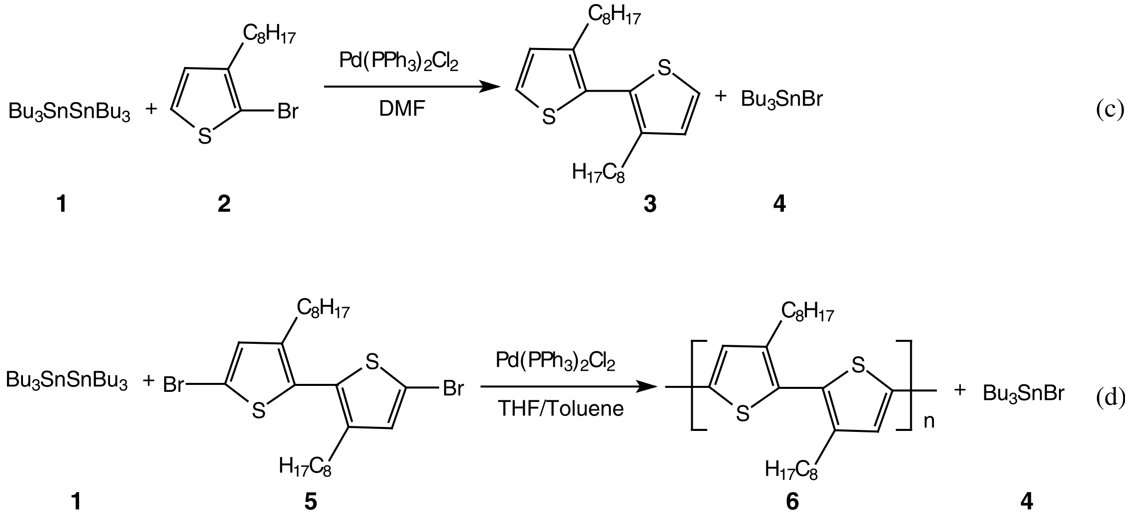
The formation of C–C bonds using the Stille cross coupling reaction is a very powerful method for the synthesis of symmetric and non-symmetric biaryl/heterobiaryl and polyconjugated systems. The reaction usually involves the cross coupling of an organic halide and an organotin compound[1–3] or self coupling of an intermediate substituted simultaneously by halogen and trialkyltin groups.[4,5] Hexaalkylstannanes, $R'_3SnSnR'_3$, were reported to react with organic halides, RX (R = aryl, allyl, benzyl and vinyl), in the synthesis of RR″ by firstly forming $RSnR'_3$ in the presence of a palladium catalyst[6–8] and then, in situ, cross-coupling of $RSnR'_3$ with another organic halide, R″X,[9] as shown in Eqs. (a) and (b):

$$RX + R'_3SnSnR'_3 \rightarrow RSnR'_3 + R'_3SnX \qquad \text{(a)}$$

$$RSnR'_3 + R''X \rightarrow RR'' + R'_3SnX \qquad \text{(b)}$$

In previous work, formation of the main product, $RSnR'_3$, in Eq. (a), was accompanied by the formation of the by-product, RR, in low yields (less than 15%).[7]

We present here a novel synthetic route to RR-type compounds in good yields and under mild conditions. We have prepared 3,3′-dioctyl-2,2′-bithiophene **3** and symmetric polymers, poly(3,3′-dioctyl-2,2′-bithiophene)s **6**, as shown in Scheme 1, Eqs. (c) and (d),



Scheme 1. The synthetic route to substituted bithiophene and polybithiophenes.

Keywords: hexabutyldistannane; palladium catalyzed; substituted thiophene; polymers containing thiophene.

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respectively. The starting materials used here are hexabutyldistannane, $Bu_3SnSnBu_3$ **1**, and 3-octyl-2-bromothiophene **2** (for dimer **3**) or 5,5′-dibromo-3,3′-dioctyl-2,2′-bithiophene **5** (for polymer **6**).

For the synthesis of bithiophene **3**, the present approach has advantages such as a higher yield, less air sensitivity and easier handling and work-up, in contrast to the conventional method reported by Iyoda et al.,[10,11] in which 3-alkyl-2-iodothiophene, activated Zn and Et_4NI are used as starting materials and THF as the solvent. It is also superior to the recently reported, nickel-catalyzed Kumada coupling of 3-alkyl-2-bromothiophene with 2-(3-alkylthienyl) magnesium bromide (alkyl = methyl, butyl, hexyl and octyl).[12] As shown in Scheme 1, Eq. (c), the typical dimerization of the substituted thiophene was achieved by reacting compound **1** (1.0 mmol) and **2** (2.0 mmol) in the presence of the palladium complex [$Pd(PPh_3)_2Cl_2$, 0.020 mmol] as a catalyst in DMF at 85°C for 24 h under nitrogen. Distillation of the black reaction mixture under reduced pressure conveniently led to, first, the removal of the solvent DMF and then, the side-product Bu_3SnBr **4**. The residue was then distilled twice using a bulb-to-bulb distillation apparatus (bp 230°C/1 mbar) to afford pure product **3** as an off-white liquid in a yield of up to 78%, which was higher than that reported by Iyoda and co-workers (35%)[10] and by Hoffmann and co-workers (52%).[12]

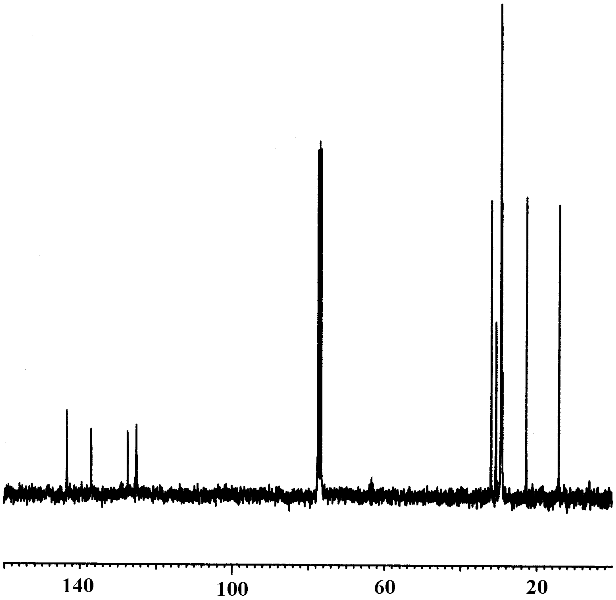
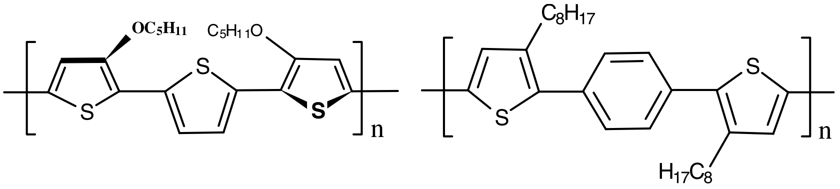


Figure 1. ^{13}C NMR spectrum of poly(3,3′-dioctyl-2,2′-bithiophene)s (**6**).

Extension of this reaction by using 5,5′-dibromo-3,3′-dioctyl-2,2′-bithiophene, **5** (prepared from **3** by bromination with Br_2 in $AcOH/CHCl_3$ in a yield of 95%), as a replacement for **2** led to the generation of substituted polybithiophenes, as illustrated in Scheme 1. Here, **1** and **5** were added in the same molar ratio (1:1) while $Pd(PPh_3)_2Cl_2$ was kept at 2 mol%. A mixture of THF/toluene (1:2) was used as the solvent instead of DMF in order to increase the solubility of product polymer in the reaction mixture and to facilitate the polymerization. The reaction was carried out at 105°C for 2 days. A solid was obtained by pouring the very dark reaction mixture into methanol, precipitating and filtering. It was subjected to soxhlet extraction with methanol and acetone to eliminate any oligomer. The residue was then extracted with chloroform and reprecipitated from methanol. A yellow solid polymer **6** was obtained at a yield of 71%, which exhibited very good solubility in chloroform and THF and had a number-averaged molecular weight (M_n) of 6800 and a polydispersity index (PDI) of 1.9 (measured by gel permeation chromatography using THF as eluent and polystyrene as standard). Its structure was confirmed by ^1H, ^{13}C NMR (shown in Fig. 1) and FTIR and is the same as that reported earlier.[10] The present method obviously bears the merits of high yields, simplicity of work-up as no de-doping effort was needed, and formation of the polymer with a narrow molecular weight distribution with reference to the $FeCl_3$ oxidation method.[10] The advantage brought by the avoiding of de-doping process might be more significant than the traditional $FeCl_3$ oxidation way in some polymer systems, such as poly(3,3″-dipentoxyterthiophene)s **7** (Fig. 2), since it was reported to be especially difficult to be de-doped.[13]

This new method was firstly discovered when a yellow solid was obtained after a mixture of 1,4-bis(5-bromo-3-octyl-2-thienyl)benzene (structure not shown), compound **1**, and a catalytic amount of $Pd(PPh_3)_2Cl_2$ in DMF was heat-treated with the aim of substituting Br with $SnBu_3$ in the molecule. This solid was then structurally elucidated to be poly[1,4-bis(3-octyl-2-thienyl)phenylene] **8** (Fig. 2) by ^1H NMR and FTIR, being the same as that produced by the $FeCl_3$ oxidation method and reported in our earlier work,[14,15] except



7 **8**

Figure 2. The chemical structures of some central symmetric polymers.

that a minor content of the $SnBu_3$ group in the polymer was indicated by its resonances in the ^1H NMR spectrum in the range of 0.8–1.5 ppm, overlapping with those of octyl group. The later observation may suggest that the reaction takes place by, firstly, the formation of $ArSnBu_3$ and then, by Stille coupling between $ArSnBu_3$ and ArBr.

In order to obtain more support for this speculation, we simply carried out the reaction leading to the synthesis of **3** (Scheme 1) at 110°C but without the palladium catalyst. The result seems to support the hypothesis as no evidence for the formation of **3** was found in the NMR spectrum even after 2 days reaction. However, further work is now under way to understand the reaction mechanism precisely and to examine the general applicability of this novel method to the synthesis of symmetric and non-symmetric biaryl/heterobiaryls and other polymers.

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