Semiconducting Polymers via Microwave-assisted Suzuki and Stille Cross-Coupling Reactions

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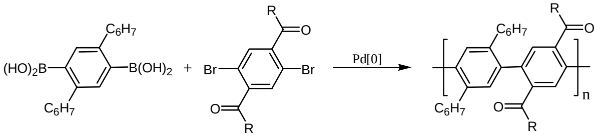
Introduction:

Recently, interest in the area of microwave-assisted chemistry has intensified, in part as it is efficient in reducing reaction times thereby allowing the fast screening of a wide range of reaction conditions.[1] Surprisingly the application of microwaves to accelerate synthetic protocols towards the preparation of high molecular weight semiconducting polymers remains relatively unexplored.[2] To our knowledge the only microwave-assisted aryl-aryl coupling polymerisation to date was reported by the IBM Almaden group and concerns the Nickel(0) mediated preparation poly(9,9-dihexylfluorene) in ca. ten minutes.[3] Herein we report that microwave heating is equally successful in the preparation of other semiconducting polymers via transition metal catalysed Suzuki and Stille coupling reactions.[4]

Suzuki-Reaction:

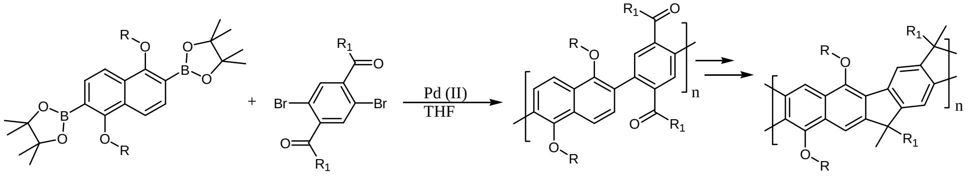
Ladder type poly(*para*-phenylene) materials (LPPP) have attracted widespread attention.[5] The standard synthetic sequence to LPPPs involves the generation of a ketone functionalised single stranded polymer via a Suzuki cross-coupling reaction. To define the optimal conditions we began with the known LPPP-precursor **P1** and then prepared a new napthalene-phenylene polyketone precursor which was cyclized to the analogous ladder polymer. Noteworthy was:
(i) M_n values and yields compare favourably with polymers prepared by conventional heating, (ii) M_n increased with time: optimum ~ 9 mins, (iii) heating was more regular when a more miscible two phase solvent system such as THF/water was used, (iv) µW power applied is important: 70, 100 and 150 W gave Mn values of 3,700, 4,200 and 12,600 respectively.



P1

$R = 1,4\text{-}C_6H_4\text{-}C_{10}H_{21}$

conv.: 3d, M_n = 12000, Pd = 1.6
MW: 12 min., M_n = 12600, Pd = 1.8



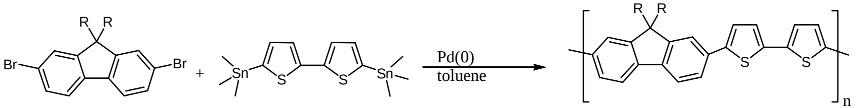
R = n-octyl

$R_1 = 1,4\text{-}C_6H_4\text{-}C_{10}H_{21}$

conv.: 3d, M_n=14200, Pd = 1.8
MW : 12 min., M_n=11300, Pd = 1.7

Stille-Reaction:

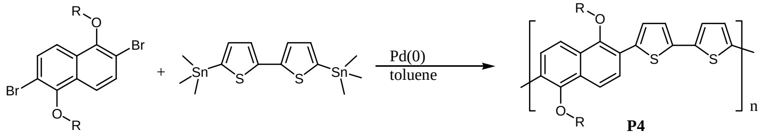
Alternating copolymers are another very important class of semiconducting materials as they offer the possibility to manipulate the opto-electronic properties of such materials. Similarly, when developing the procedure for the Stille reaction we worked with a known system **P3**.[6] With his cross-coupling protocol: (i) only appreciable degrees of polymerisation when power levels greater than 170 W were applied, (ii) an impressive increase in both the yield and M_n for **P4** when we switched to our the microwave-assisted format .



R = ethylhexyl

P3

conv.: 3d, M_n = 12000, Pd = 1.6
MW:9 min., M_n = 15400, Pd = 1.6



R = n-octyl

P4

conv.: 3d, M_n = 5000, Pd = 2.8
MW:9 min., M_n = 13700, Pd = 3.1

Conclusions:

(i) reaction parameters such as time and applied power need optimization for each specific coupling reaction, (ii) compared to conventional synthesis, reaction times are reducible by several orders of magnitude, (iii) the yields and molecular weights of the polymers are similar between both methods of heating however in some cases there is enhanced yield and molecular weight *e.g.* **P4**.

Polymer	MW		Conv.	
	Mn	Y	Mn	Y
P1	12600	61%	12000	62%
P2	11300	72%	14200	60%
P3	15400	52%	12000	72%
P4	13700	52%	5000	34%

References:

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