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Microwave-accelerated synthesis of lengthy and defect-free poly(*m*-phenyleneethynylene)s *via* AB′ and A_2 + BB′ polycondensation routes†

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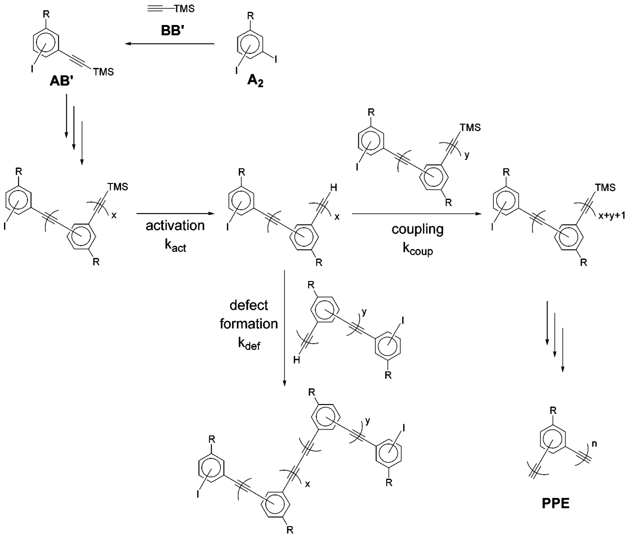
A novel microwave-assisted polycondensation protocol involving an *in-situ* activation/coupling scheme has been developed and applied to the preparation of lengthy poly(*m*-phenyleneethynylene)s without diyne defects *via* either AB′ or A_2 + BB′ approaches.

Oligo(phenyleneethynylene)s (OPE) and poly(phenyleneethynylene)s (PPE) represent attractive building blocks for the generation of functional nanostructures. While the *para*-linked OPE[1] and PPE[2] combine a linear architecture with interesting optoelectronic properties, *meta*-connected OPE have been explored in a variety of kinked and branched topologies including foldamers,[3] macrocycles,[4] and dendrimers.[5] Despite the exciting progress made in the development of palladium-catalysed alkynylation[6] as well as acyclic diyne metathesis (ADIMET) polymerisation,[2,7] defect-free PPE having high degrees of polymerisation (DP) are still difficult to prepare, in particular in the *meta*- and *ortho*-connected forms.[8] It should be noted that the absence of diyne defects is crucial to both control over secondary structure[3] as well as stability of the material.

Here, we describe a new approach to access lengthy poly(*m*-phenyleneethynylene)s (P*m*PE) having no diyne defects.[9] Our concept (Scheme 1) involves a rate-limiting *in-situ* deprotection step to minimize the concentration of free terminal acetylene in the polymerisation mixture and therefore limit competing side reactions such as bimolecular diyne defect formation. This one-pot activation/coupling procedure can be carried out starting from either AB′ monomers, which inherently are stoichiometrically balanced, or A_2 monomers in combination with commercially available trimethylsilylacetylene (TMSA)[10] as the BB′ monomer.[11]



Scheme 1 Defect-free PPE by *in-situ* activation/coupling sequence starting from either AB′ or A_2 + BB′ monomers.

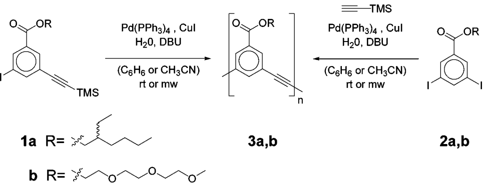
Most importantly, the reaction conditions[12] are mild and tolerant of most functional groups allowing for the preparation of a variety of functional P*m*PE derivatives.[13] Particularly noteworthy are the low temperatures required for the reaction in combination with microwave acceleration.[14,15]

In order to develop suitable polycondensation conditions, two pairs of AB′ monomers (**1a,b**) and A_2 monomers (**2a,b**) carrying non-polar, racemic 2-ethylhexyl as well as polar triethylene glycol side chains were synthesised (Scheme 2).†

In the initial thermal polycondensation reactions, several parameters were varied to test for suitability of the method and to obtain a reasonable starting point for further optimisation. It was found that the use of a freshly prepared $Pd(PPh_3)_4$ catalyst gave superior results as compared to other sources for the catalytically active $Pd^{(0)}$-species such as $Pd(PPh_3)_2Cl_2$ or $Pd_2(dba)_3$. A catalyst loading of 6 mol% was found to be optimal. Furthermore, the amount of added water, necessary to deprotect the silylated acetylene, was increased to 1.0 equiv. as compared to the substoichiometric amount of 0.4 equiv. used in the original procedure.[12]

In a subsequent focused screening of reaction conditions, AB′ monomers **1a,b** were polymerised (Table 1, entries 1–12) to allow for runs on a small scale while maintaining the necessary stoichiometric balance. Polycondensation of **1a** at room temperature in benzene yielded **3a** with an expected[2] DP = 20 (entry 1). However, microwave irradiation did not accelerate the reaction (entry 2) presumably due to the low dipole moment of the solvent used. Since the initial one-pot procedure[12] gave excellent results not only in benzene but also in acetonitrile as a polar solvent, we subsequently focused on monomer **1b** in order to explore microwave-accelerated polycondensation chemistry.[15] During the polycondensation of **1b** in acetonitrile at room temperature it was found that further increasing the water content gave rise to significantly increased chain lengths (entries 3–5). Turning to microwave-accelerated conditions reduced the reaction times considerably. In addition, temperature, time, and concentration were varied showing the expected effects on the outcome of the polycondensation (entries 6–12). The resulting, optimised polycondensation conditions involve the use of 10 equiv. of water, microwave irradiation at 40 °C for 4 h, and the use of a highly concentrated reaction mixture to afford polymers **3b** with respectable chain-lengths (DP ~ 80) and polydispersities (PDI) typical for polycondensation reactions.

Extending the concept to A_2 monomers, **2a** and **2b** were subjected to the polycondensation conditions in the presence of an equimolar amount of TMSA (entries 13 and 14). Again, microwave heating yielded superior results giving polymer **3b** with a respectable DP and PDI. Due to the commercial availability of TMSA and the rapid synthetic access to aryl diiodides, this A_2 +



Scheme 2 P*m*PE *via* AB′ and A_2 + BB′ polycondensation approaches.

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† Electronic supplementary information (ESI) available: monomer syntheses, polycondensation procedures, and polymer characterization. See http://www.rsc.org/suppdata/cc/b3/b312762a/

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Table 1 Selected polycondensation experiments according to AB′ and A_2 + BB′ approaches illustrated in Scheme 2[a]

Entry	Monomer	H_2O/equiv.	T/°C	t/h	M_w[b]	M_n[b]	PDI[b]	DP (P_n)[b]	Yield[c] (%)
1	**1a**	1	25	72	9300	5200	1.78	20	94
2	**1a**	1	40 (mw)[d]	1	5500	3800	1.44	15	83
3	**1b**	1	25	72	16200	9500	1.71	33	88
4	**1b**	4	25	72	29100	10000	2.85	35	55
5	**1b**	10	25	72	44800	20100	2.23	69	60
6[e]	**1b**	1	40 (mw)	8	14300	8700	1.64	30	59
7[e]	**1b**	2	40 (mw)	4	20300	14000	1.45	48	70
8[e]	**1b**	2	40 (mw)	8	61000	16300	3.74	55	51
9[e]	**1b**	4	50 (mw)	15	63900	17600	3.63	61	81
10[e]	**1b**	4	60 (mw)	15	52000	23300	2.23	80	39
11[e]	**1b**	10	30 (mw)	15	44400	23000	1.93	79	88
12[e,f]	**1b**	10	40 (mw)	4	62000	22800	2.71	78	85
13	**2a**	1	25	72	9300	5200	1.78	20	94
14	**2b**	1	40 (mw)	4	31400	18500	1.69	64	80

[a] Conditions: 1 equiv. AB monomer (**1a,b**), 6 mol% $Pd(PPh_3)_4$, 6 mol% CuI, 6 equiv. DBU in 4 mL of solvent (C_6H_6 for **1a**, **2a** and CH_3CN for **1b**, **2b**); in the case of A_2 monomers (**2a,b**), 1 equiv. TMSA was added as well. [b] According to GPC in THF at 40 °C. [c] Isolated yield after precipitation into MeOH (**1a**,**2a**) or Et_2O (**1b**,**2b**) and short silica column in CH_2Cl_2. [d] Microwave heating. [e] GPC in NMP containing 0.5 wt% LiBr at 70 °C. [f] In 3.3 mL of CH_3CN.

BB′ approach has great potential for the preparation of various PPE derivatives on a large scale.

In most cases, monomer conversion is almost quantitative, however, a considerable amount (up to 26% by GPC) of low molecular weight compounds, presumably oligomeric macrocycles, is being formed as well. In the case of amphiphilic polymer **3b**, some material is inevitably lost during precipitation into diethyl ether. Hence, the isolated yields range from 83–94% for **3a** to 39–88% for **3b**.

The resulting polymers were thoroughly analysed by ^{13}C-NMR spectroscopy in order to detect potential diyne defects. In polymer **3b**, such a defect would give rise to two characteristic signals at: $80.6 \geq \delta \geq 79.7$ and $75.4 \geq \delta \geq 74.7$ ppm as indicated by ^{13}C-NMR spectral data of diacetylene-linked oligomers having the exact same substitution pattern.[16] Gratifyingly, even after extensive scanning of concentrated samples no signals that could be attributed to diyne defects were found while the acetylene carbon is clearly visible at $\delta \sim 89$ ppm (Fig. 1).

Both the absence of diyne defects as well as the observed strong dependence of polymer chain length on the water content indicate the validity of our initial working hypothesis (Scheme 1) where deprotection represents the rate-limiting step. Further insight into polycondensation kinetics was obtained using an *in-situ* ^{1}H-NMR experiment that points to fast deprotection and coupling steps leading to the rapid build-up of short oligomers typical for polycondensation processes.†

Ongoing work in our laboratories is focused on expanding the scope of the synthetic route outlined herein as well as evaluating both folding and aggregation behavior of amphiphilic P*m*PE.

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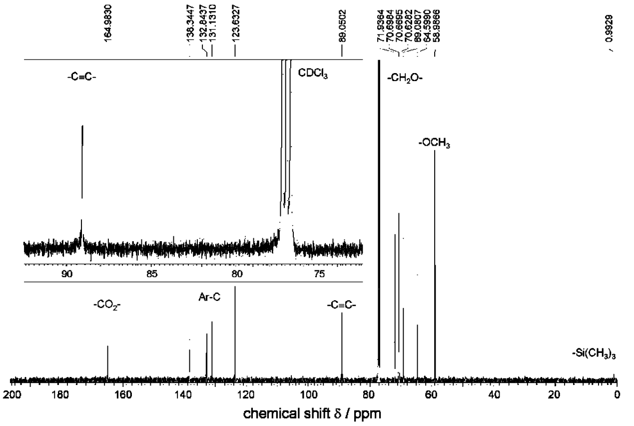

Fig. 1 ^{13}C-NMR spectrum of P*m*PE **3b** (126 MHz, 116459 scans, $CDCl_3$, 25 °C). The inset shows the region of potential diacetylene defects.[16]

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