

Chapter 2

Synthesis of Lengthy and Defect-Free Poly(*meta*-phenylene ethynylene)s

A novel polycondensation protocol involving an *in-situ* activation/coupling scheme has been developed and applied to the preparation of lengthy poly(*m*-phenylene ethynylene)s without diyne defects via either AB' or A₂+BB' approaches.

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Introduction

Oligo(phenylene ethynylene)s (OPE) and poly(phenylene ethynylene)s (PPE) represent attractive building blocks for the generation of functional nanostructures. While *para*-linked OPE^[1] and PPE^[2] have attracted significant attention due to their unique properties and potential applications in molecular electronics and sensor technologies, their *meta*-linked counterparts have received relatively less attention. Moore and co-workers have recently described amphiphilic *meta*-linked OPEs and their ability to fold into helical conformation in solution.^[3] The helical secondary structure in polar organic solvents such as acetonitrile is driven by segregation of the polar triglyme side chains and the non-polar phenylacetylene scaffold and directed by the *meta*-connectivity of the backbone and π,π -stacking interactions between aromatic moieties in adjacent turns. A series of oligomers from dimer through octadecamer was prepared and a detailed investigation revealed the chain length dependence on folding behaviour of these oligomers. Starting at the dodecamer, the helix-coil transition both sharpens and shifts to larger amounts of denaturant for higher oligomers.^[4] Quantitative analysis shows a linear relationship between chain length and helix stabilization energy as expected by the helix-coil theory.^[5]

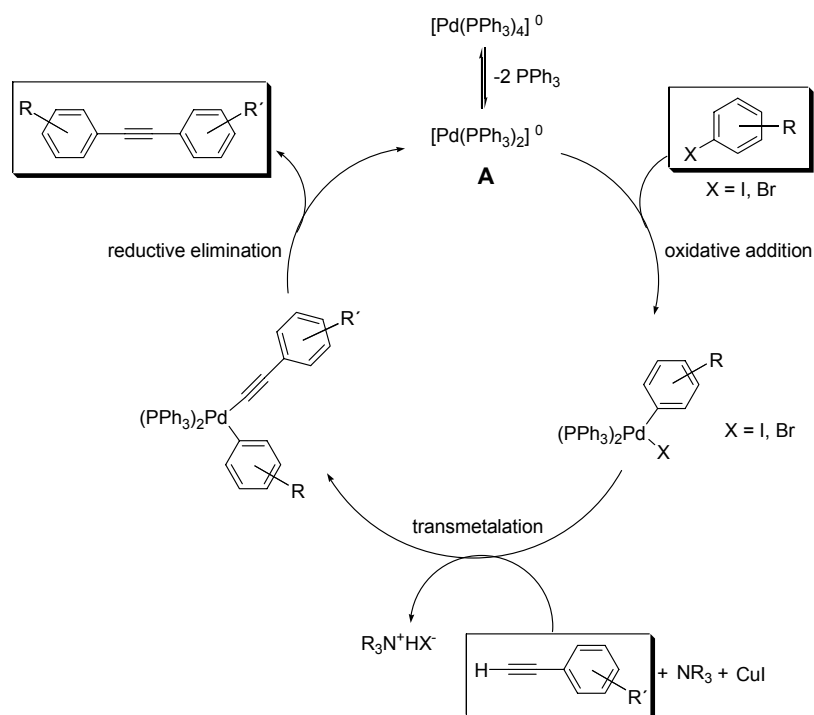
On one hand where synthesis of discrete and well defined oligomers is important to evaluate the properties and the behavior of a system correctly, on the other, step wise synthesis and purification of these oligomers is a tedious and time consuming process. An alternative approach is the polymerization of readily synthesized monomers. This method allows to study

many different kinds of systems in comparably little time. We were interested in synthesizing high molecular weight *meta*-linked PPEs to exploit the folding property of these polymers in order to create organic nanotubes of controlled dimensions and functionality (see Chapter 3). However, a quick glance at the literature revealed that the synthesis of high molecular weight *meta*-linked PPEs is still difficult. The reported degree of polymerization (DP) for different *meta*-linked PPEs ranges from 6 to 28.^[2] In fact there is only one example where *meta*-linked PPEs with Mn of 17800 corresponding to ~ 80 repeat units could be synthesized.^[6] Bunz's acyclic diyne metathesis (ADIMET) polymerization is known to yield PPEs of very high molecular weights but low tolerance of functional groups and harsh reaction conditions (130-150 °C) severely limits this method.^[7]

Synthesis of high molecular weight PPEs by Sonogashira-Hagihara polycondensation

The protocols that allow the C-C bond formation are very vital in organic synthesis. Sonogashira-Hagihara^[8] reaction is perhaps the most frequently used method to create C-C bond. It involves the cross coupling of either an aryl halide (mostly bromide or iodide) with a terminal alkyne under palladium-catalyzed conditions. Palladium complexes are possibly the most versatile C-C bond forming catalysts for several reasons: i) Pd has a marked preference for the 0 and +2 oxidation states, thus facilitating regeneration of catalytically active palladium species, ii) it is reluctant to undergo radical processes thus avoiding unwanted side reactions, iii) it has very wide functional group tolerance that allows use of many different kinds of substrates. Scheme 1 shows the catalytic cycle involved in the Sonogashira-Hagihara cross-coupling reaction. The first step is the oxidative addition of an aryl halide to the catalytically active palladium (0) species (A) followed by transmetalation and reductive elimination to give the cross-coupled product.

Scheme 1



Several factors influence the coupling reaction, which are of little concern in synthesis of small organic molecules. However, special care is necessary in choosing the conditions for synthesizing high molecular weight polymers. We will discuss some of them briefly.

Choice of the halide

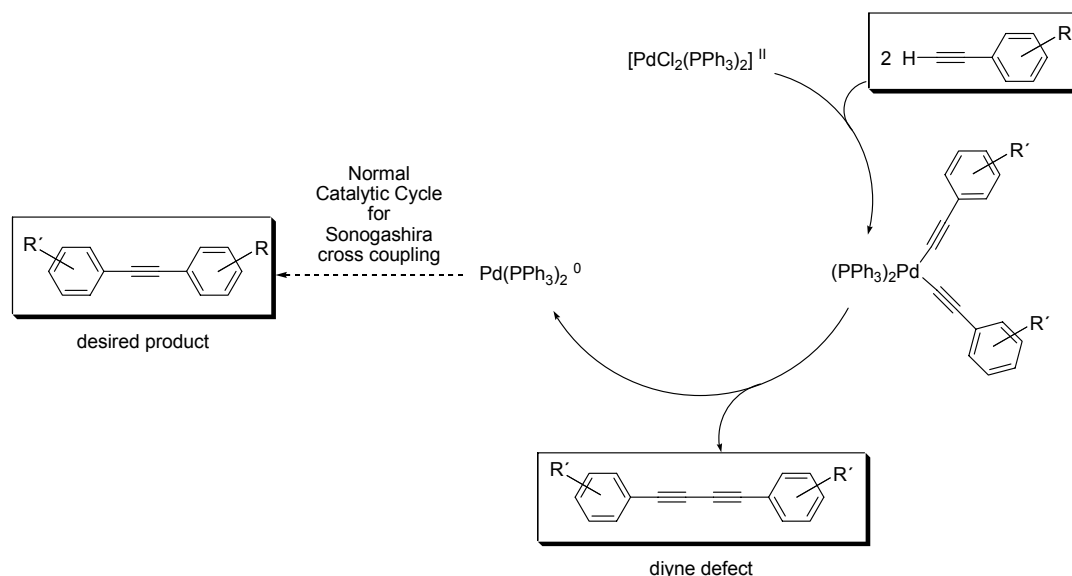
Aryl iodides or bromides can be used as coupling partners in the synthesis of polymers but there is a significant difference in the reactivity of aryl iodides and aryl bromides. Aryl iodides are known to be more reactive than aryl bromides due to their lower bond dissociation energy. Hence reactions involving aryl bromides need high temperatures, while aryl iodides react at room temperature. This is quite important for a polymerization reaction as lower temperatures will prevent side reactions to occur and decrease the number of structural defects in the polymer. The high reactivity of aryl iodides results in better yields for each coupling step hence polymers with a higher degree of polymerization can be obtained.

Catalyst

The choice of the catalyst obviously has a marked influence on the final result of polymerization reaction. For many years, Pd (II) catalyst $Pd(PPh_3)_2Cl_2$ was used mostly because of its air stability relative to the palladium (0) catalysts, such as $Pd(PPh_3)_4$ or $Pd_2(dba)_3$, but

synthesis of high molecular weight polymers by using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ were found to be difficult. This is attributed to the initiation of the catalytic cycle. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ consumes some amount of aryl alkyne to form catalytically active palladium (0) species (Scheme 2). This causes an imbalance of the stoichiometry, finally resulting in low molecular weight oligomers. Hence palladium (0) catalyst is desirable for the synthesis of high molecular weight polymers.

Scheme 2



Choice of substituent on aryl halide

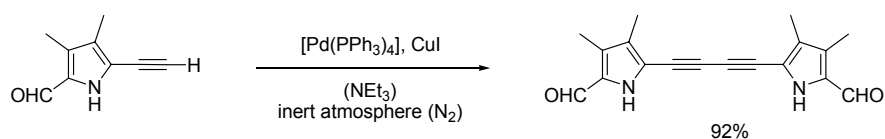
The oxidative addition involves an electron rich palladium (0) species (A) hence more electron deficient aryl halide react faster than their electron-rich counterparts. Therefore, electron withdrawing groups accelerate the reaction resulting in increased yields and high molar masses. The other important role of the substituent is to impart solubility to the growing polymer chain in the reaction medium thereby maintaining the homogeneous process of chain propagation and finally, helping to solubilize the polymer for purification, characterization, and further applications. It should be noted that early attempts to prepare PPEs resulted in formation of insoluble and infusible material due to the lack of any solubilizing substituents on the repeat unit.

Solvent

A number of different kinds of bases are used in the coupling protocol with a co-solvent. The addition of a co-solvent is very important as it keeps the growing polymer chain dissolved in the reaction medium thereby allowing the chain propagation to proceed. In the absence of such

protocol (Scheme 2). Even if palladium (0) species are used, the copper acetylide species (Scheme 1, C) involved in the catalytic cycle can dimerize the alkyne in presence of little oxygen (Glaser coupling). The absence of Cu makes the reaction very sluggish yet it can't be avoided. Most importantly, even if oxygen is rigorously excluded from the reaction mixture, the Pd (PPh₃)₄ is known to catalyze the dimerization of alkyne in excellent yields in inert atmosphere^[10] (Scheme 4).

Scheme 4



Therefore, we envisioned that the best way to avoid this problem was to keep the concentration of free acetylene in the reaction mixture as low as possible. One possibility to realize this is the slow addition of the free acetylene to the reaction mixture but this could lower the reproducibility of the polymerization. The other way is the *in-situ* deprotection of the protected acetylene monomer.^[11]

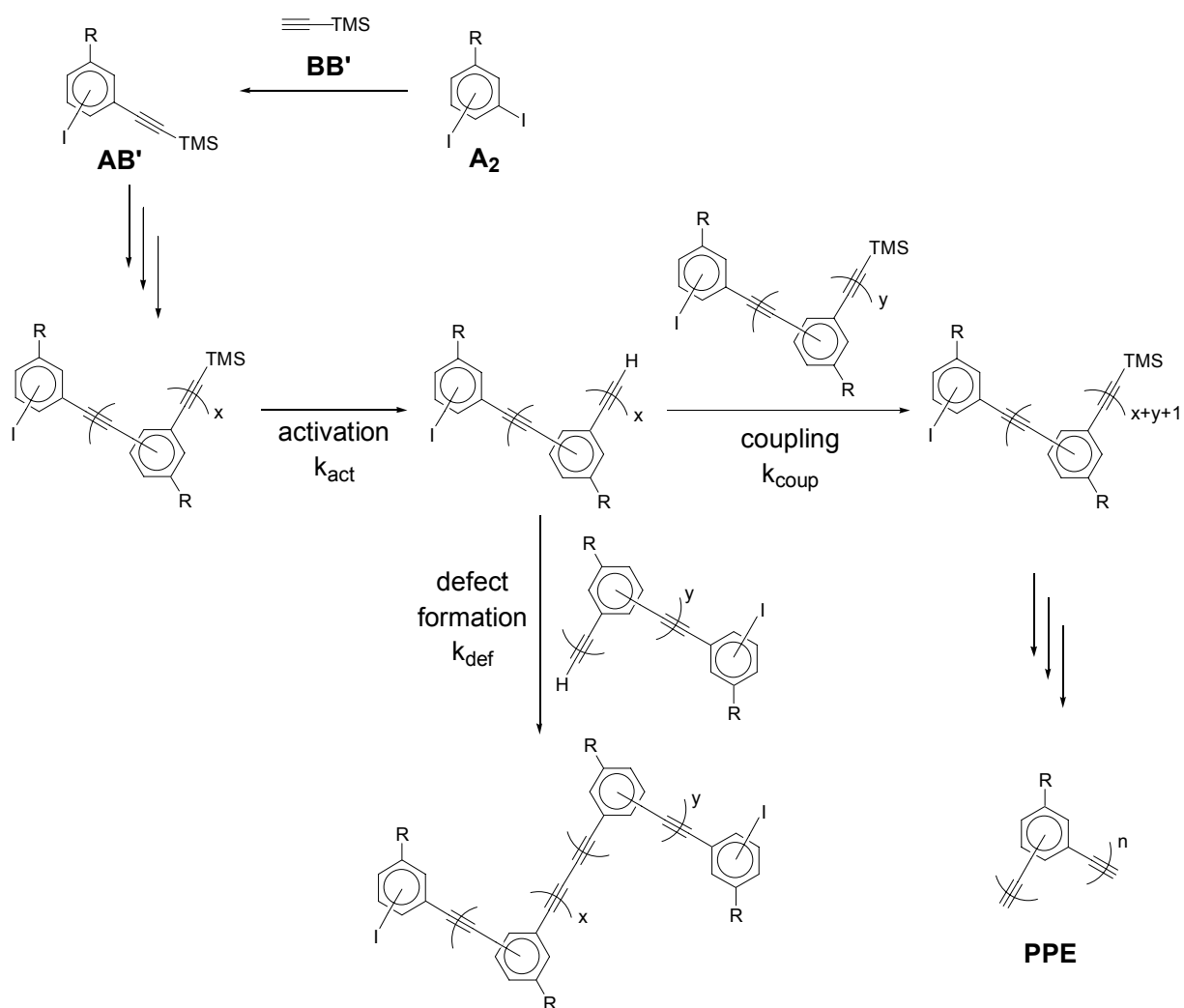
Motivation

Here, we aimed to develop a practical method to access high molecular weight *meta*-linked PPEs. We choose palladium-catalyzed coupling due to their requirement of mild reaction conditions. A variety of *Pm*PE derivatives with diverse functionalities can be synthesized this way. However, the task of overcoming the formation of diacetylene defects associated with the coupling reaction was challenging. Few examples found in literature also motivated us to investigate in this area.

Synthesis of lengthy and defect free *Pm*PEs by *in-situ* deprotection and coupling protocol

Our concept (Scheme 5) involves a rate-limiting *in-situ* deprotection of TMS protected acetylene monomer to minimize the concentration of free acetylene in the polymerization mixture. The low concentration of free acetylene minimizes the chances of catalytic homocoupling of acetylene monomer and oxidative coupling of copper acetylide. Under these conditions ($k_{\text{coup}} \gg k_{\text{def}}$) the unwanted side reaction can be restricted.

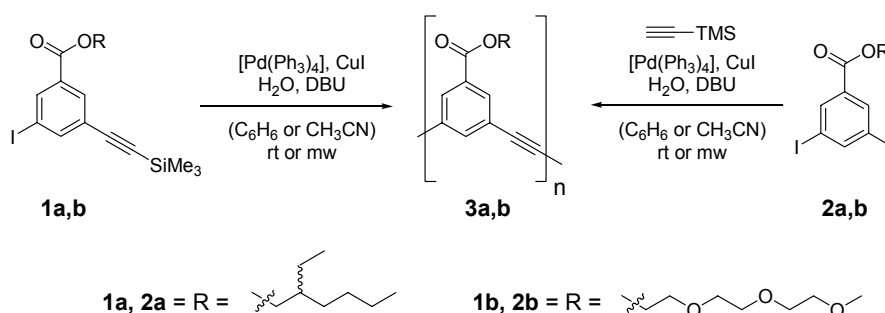
Scheme 5



Monomer and Polymer Syntheses

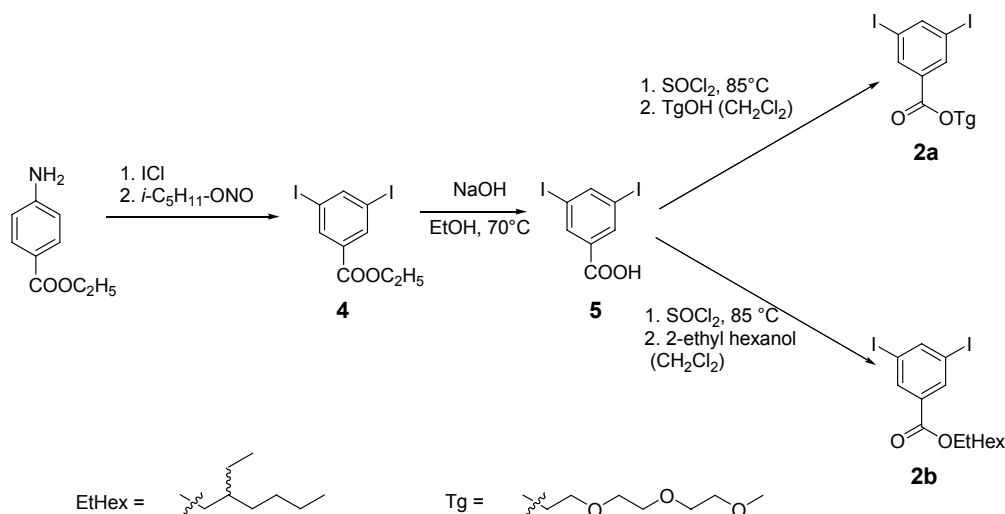
In order to develop suitable polycondensation conditions, two pairs of AB' monomers (**1a,b**) and A_2 monomers (**2a,b**) carrying non-polar, racemic 2-ethylhexyl as well as polar triethylene glycol side chains were synthesized (Scheme 6).

Scheme 6



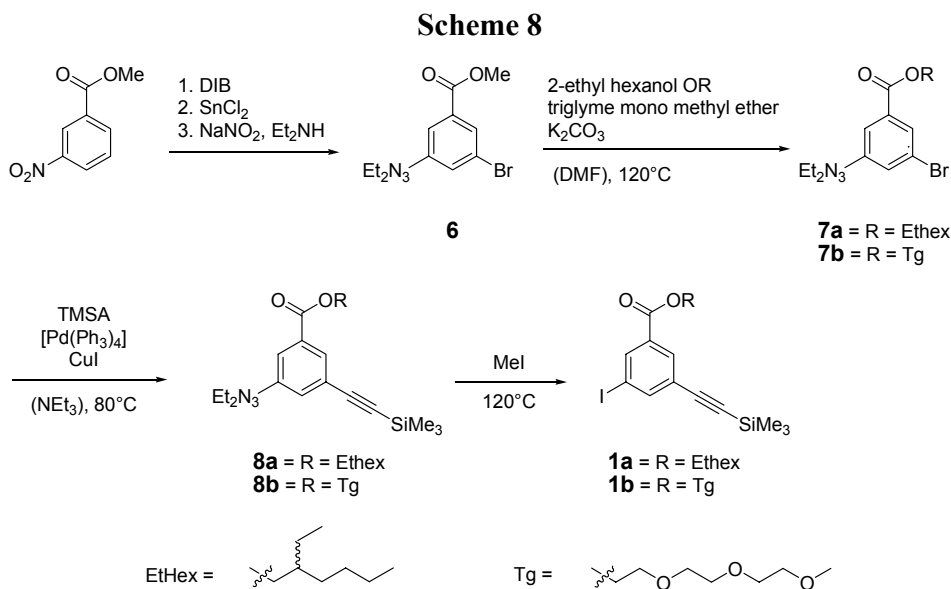
Synthesis of A₂ monomers starts with iodination of ethyl-4-aminobenzoate followed by deamination and saponification to yield the corresponding 3,5-diiodobenzoic acid. This rather insoluble acid was dissolved in boiling thionyl chloride and the resulting acid chloride was esterified with 2-ethylhexanol and triethylene glycol monomethyl ether to give non-polar (**2a**) and polar (**2b**) monomers, respectively (Scheme 7).

Scheme 7



Synthesis of AB' monomers is based on 3-nitromethyl benzoate. This electron poor aromatic substrate was brominated with the help of Dibromoisocyanuric acid (DIB) followed by reduction and protection of the resulting aniline as a triazene moiety. Trans-esterification with 2-ethylhexanol and triethylene glycol monomethyl ether furnished compounds **7a** and **7b**, respectively. Palladium-catalyzed coupling of TMSA followed by conversion of the triazene to

an iodide in boiling methyl iodide furnished the AB' nonpolar (**1a**) and polar^[16] (**1b**) monomers (Scheme 8).



Two approaches namely AB' and A₂+BB' have been used for carrying out polycondensation reactions. A refers to aryl iodide, B refers to free terminal acetylene, and B' to TMS-protected terminal acetylene moieties. Both approaches have advantages and disadvantages. The A₂+BB' approach involves diiodide monomers (**2a** or **2b**) and TMSA as coupling partners while the merit of this approach lies in the rapid synthesis of A₂ monomers and the commercial availability of the BB' monomer (TMSA), the two monomers have to be used in strictly equal molar amounts in the polycondensation reaction. This stoichiometric balance is very important in step growth polymerization to achieve high molecular weights. Hence the two monomers should be more than 99.5% pure to calculate the needed amount correctly and then it should be weighed and loaded with utmost care to increase the chances of a successful polycondensation reaction. On the contrary, the use of an AB' monomer, needs no such efforts as functional groups in this monomer are intrinsically balanced, however synthesis of the AB' monomers is more tedious as compare to A₂ monomers.

In the initial thermal polycondensation reactions, monomer **2a** was used and several parameters were varied to test the suitability of the method and to obtain a reasonable starting point for further optimization. Three different catalyst system were used and it was found that the use of a freshly prepared Pd(PPh₃)₄ catalyst gave superior results as compared to other sources

for the catalytically active Pd⁽⁰⁾-species such as Pd(PPh₃)₂Cl₂ or Pd₂(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] An excess of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) was used in all the experiments. In a subsequent focused screening of reaction conditions, AB' monomers **1a,b** were polymerized (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.^[13] 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, optimized 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.

Table 1 Selected polycondensation experiments according to AB' and A₂+BB' approaches illustrated in Scheme 6.^a

entry	monomer	H ₂ O / equiv.	T / °C	time / 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(PPh₃)₄, 6 mol% CuI, 6 equiv. DBU in 4 mL of solvent (C₆H₆ for **1a**, **2a** and CH₃CN for **1b**, **2b**); in case of A₂ 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 Et₂O (**1b,2b**) and short silica column in CH₂Cl₂; ^d microwave heating ^e GPC in NMP containing 0.5 wt% LiBr at 70 °C, ^f in 3.3 mL of CH₃CN.

Extending this concept to A₂ monomers, **2a** and **2b** were subjected to the polycondensation conditions in the presence of an equimolar amount of TMSA (entries 13,14). 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 A₂+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**.

Polymer Characterization

Several analytical techniques have been used for polymer characterization. All samples were purified by single precipitation and were non-fractionated. Currently, we are fractionating these and related polymers generated by this method to investigate the influence of molecular weight on polymer properties.

Polymers **3a** and **3b** were thoroughly analyzed by ^{13}C -NMR spectroscopy in order to detect potential diyne defects. In polymer **3b**, such 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.^[14] 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 (Figure 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 5) where deprotection represents the rate-limiting step.

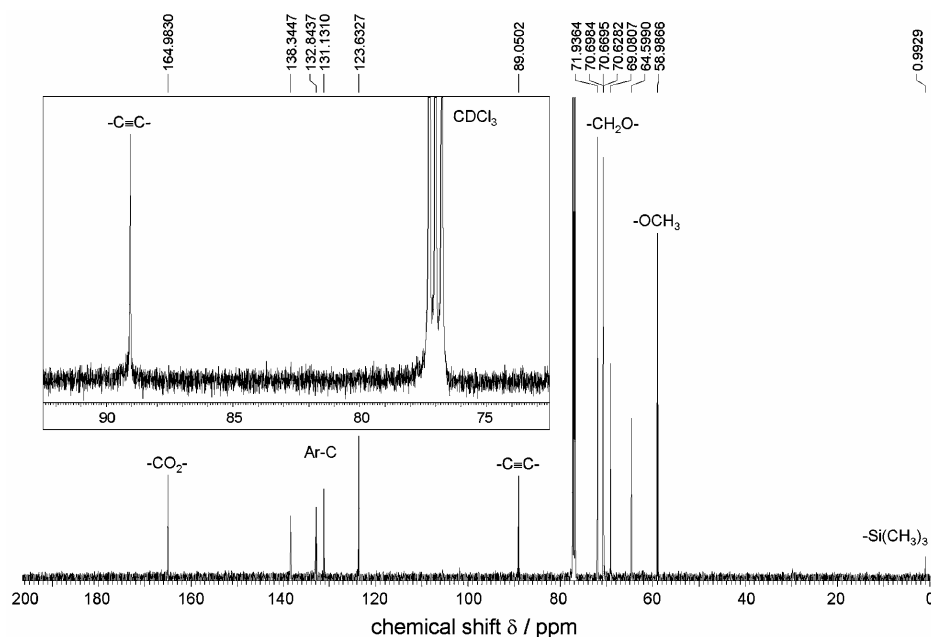


Figure 1. ^{13}C -NMR spectrum of polymer **3b** (126 MHz, 116459 scans, CDCl_3 , 25 °C). The inset shows the region of potential diyne defects.

Figure 2 shows the $^1\text{H-NMR}$ spectra of polymer **3a** (left) and **3b** (right). Broad signals in the aromatic and aliphatic regions are clearly discernable. Absence of signals from the end groups suggests that the polymers are of high molecular weight.

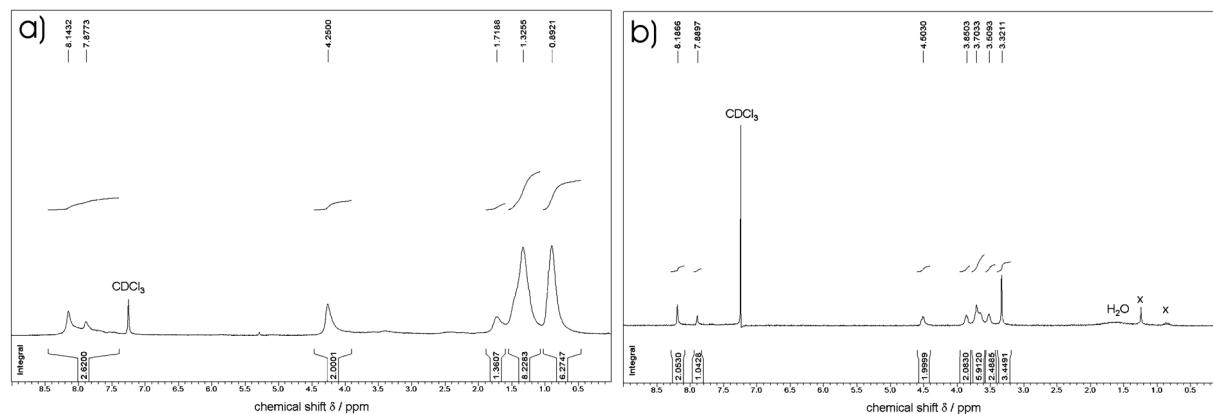


Figure 2. $^1\text{H-NMR}$ spectra of: a) polymer **3a** and b) polymer **3b** (250 MHz, CDCl_3 , 25 $^\circ\text{C}$).

Polycondensation kinetics were studied using an *in-situ* $^1\text{H-NMR}$ experiment. The AB' procedure was monitored by $^1\text{H-NMR}$ spectroscopy using CD_3CN as the solvent. After acquisition of the initial spectrum, DBU and water were added to initiate deprotection and hence polycondensation. After addition, $^1\text{H-NMR}$ spectra were taken at given time intervals (Figure 3). The deprotection can be followed by shift of TMS-signal, indicative of TMS-group transfer while coupling can be monitored either in the aromatic or triglyme regions of the spectrum by the build-up of new peaks and increasing peak broadening caused by the formation of oligomers and polymers. A signal corresponding to free terminal acetylene (expected at $\delta \sim 3.17$ ppm) cannot be detected due to the overlapping of the intense DBU signal.

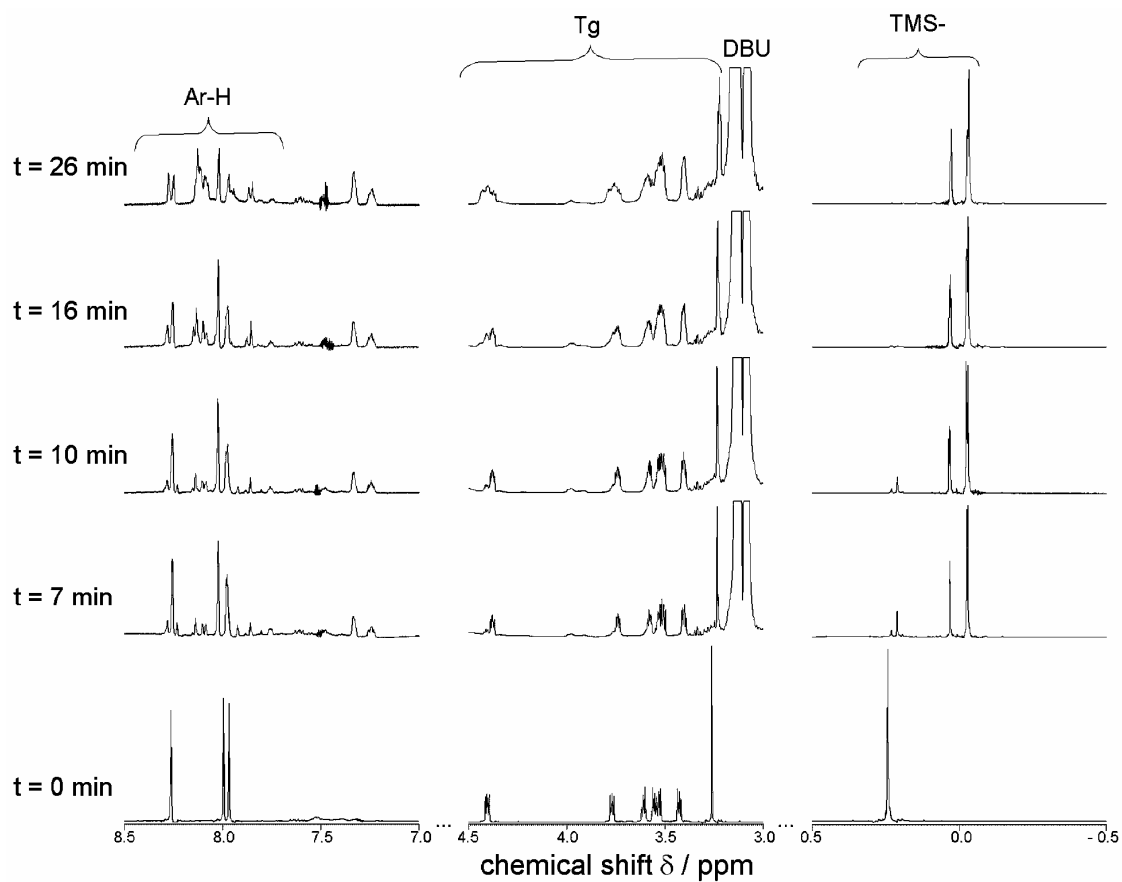


Figure 3. *In-situ* ^1H -NMR experiment following the AB' polycondensation of monomer **1b**. Representative regions diagnostic for aromatic, triglyme, and trimethylsilyl protons are shown at the given time intervals.

A typical monomodal gel permeation chromatogram of polymer **3b** in THF can be seen in Figure 4. This polymer was synthesized via $\text{A}_2+\text{BB}'$ polycondensation in 4 hours by using microwave irradiation (Table 1, entry 14). The polymer was purified by a single precipitation in diethyl ether.

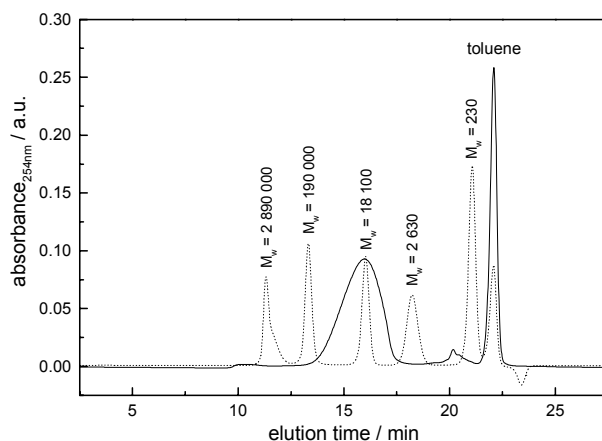


Figure 4. GPC trace of polymer **3b**. The polystyrene standards used for calibration and their respective molecular weights are shown (·····).

The UV-vis spectra of polymer **3b** (Figure 5) in chloroform exhibit two absorption maxima at 290 and 304 nm. These two bands can be regarded as two vibronic structures belonging to the *cisoid* and *transoid* conformation of phenylacetylene chromophore. In acetonitrile, however the 304 nm band vanishes completely and the other band shifts to 282 nm. This indicates the solvophobic collapse of these polymers from a random coil conformation to a compact helical conformation in polar solvent. The absorption spectra of polymer **3b** (Figure 5, left) share the same features as polymer **3b** in chloroform.

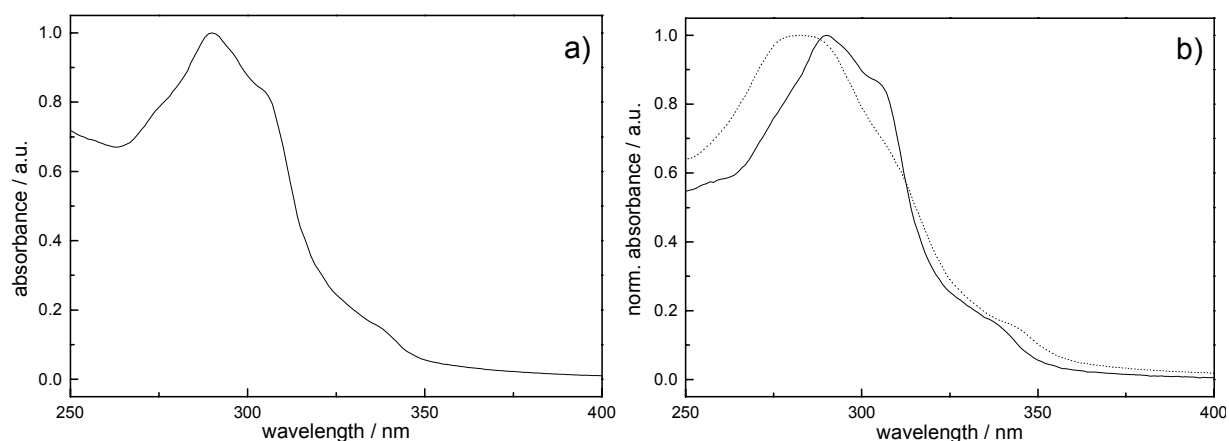


Figure 5. UV/vis absorption spectra of: a) polymer **3a** in CHCl_3 (—) and b) polymer **3b** in CHCl_3 (—) and CH_3CN (·····) (25 °C).

Conclusion

We have synthesized lengthy and defect-free *meta*-linked PPEs by novel *in-situ* activation/coupling protocol. Two approaches, AB' and A₂+BB' have been used. Microwave irradiation has been shown to accelerate the polycondensation reaction and hence the time period of a polycondensation can be significantly reduced. The developed A₂+BB' approach can in principle be utilized to generate many different kinds of PPE structures on a large scale because of facile easy monomer synthesis and commercial availability of TMSA.

With this method in hand, other linkage geometries, i.e. *ortho*- PPEs (Chapter 3) and *para*- PPEs (Chapter 6) have been synthesized for investigating both conformational and optical properties of these polymers. In addition, synthesis and post-functionalization of a *meta*-linked PPE derivative by intramolecular crosslinking has been achieved to create covalently stabilized tubular nano-objects (Chapter 4).

Experimental Section

General Methods

Compounds **4**,^[15] **6**,^[16] and monomer **1b**^[16] were synthesized as described in the literature. Pd(PPh₃)₄ was freshly prepared,^[17] all other chemicals were commercial and used as received. Benzene and acetonitrile were distilled prior to use under N₂ atmosphere over sodium/benzophenone ketyl and calcium hydride, respectively. Microwave-assisted polycondensations were performed in a Thomtec (type MTW – O) microwave reactor, which monitors the sample temperature by IR and automatically adjusts the microwave power to maintain the programmed temperature. All the reactions were carried out at 60 % microwave power, i.e. 600 W. Column chromatography was carried out with 130-400 mesh silica gel. NMR spectra were recorded on Bruker AB 250 (250.1 and 62.9 MHz for ¹H and ¹³C, respectively) and AC500 as well as Delta JEOL Eclipse 500 (500 and 126 MHz for ¹H and ¹³C, respectively) spectrometers at 23 ± 2 °C using residual protonated solvent signal as internal standard (¹H: δ(CHCl₃) = 7.24 ppm, δ(DMSO) = 2.49, δ(CH₃CN) = 1.94 ppm and ¹³C: δ(CHCl₃) = 77.0 ppm, δ(DMSO) = 39.7 ppm). Mass spectrometry was performed on Perkin-Elmer Varian Type MAT 771 and CH6 (EI) or Type CH5DF (FAB) instruments. UV/visible absorption spectra were recorded in spectroscopic grade chloroform and acetonitrile, respectively, using quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer equipped with a Peltier thermostated cell holder (T = 25 ± 0.05 °C). IR spectra were recorded as KBr pellets on a Nicolet 5SXC FTIR-Interferometer. Elemental analyses were performed on a Perkin-Elmer EA 240. GPC measurements in THF as the mobile phase were performed on a Waters 515 HPLC pump-GPC system equipped with a Waters 2487 UV detector (254 nm detection wavelength) at 40 °C using a flow rate of 1 mL/min. The samples were separated through Waters Styragel HR1 or HR3 columns with 5 μm bead sizes, which were calibrated with several narrow polydispersity polystyrene samples using an internal toluene standard. GPC measurements in 0.5 wt % LiBr in NMP as the mobile phase were performed on a Thermo Separation Products SEC setup equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors at 70 °C using a flow rate of 1 mL/min. The column set employed was 300 x 0.8 cm, 10 μm PSS-GRAM: 30, 30, 100, 3000 Å. The columns were calibrated with several narrow polydispersity polystyrene samples. The HPLC system consisted of a Knauer Eurosphere 7μm C18, 4·120 mm silica gel column and UV-detection at 254 nm with an eluent flow of 1 mL/min.

Monomer synthesis

3,5-Diiodobenzoic acid (5):^[18] Compound **A**^[15] (1.6 g, 4 mmol) was dissolved in ethanol (5 mL) and 1 M aq. NaOH (20 mL), the solution was refluxed for 2 h at 70 °C, then allowed to cool to rt, and neutralized with 1 M HCl. The white precipitate that appeared immediately was filtered and washed with water followed by recrystallization from ethanol furnishing 1.3 g of the product as a white solid (87 % yield). Characterization data agreed with the literature.^[18]

2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethyl 3,5-diiodobenzoate (2b): Compound **B** (4.7 g, 12mmol) was mixed with thionyl chloride (50 mL) and refluxed for 2 h. Excess thionyl chloride was removed *in vacuo* and the remaining residue was dried on a vacuum pump for 3 h to afford the crude acid chloride as a white solid. It was then added to a stirring solution of triethylene glycol monomethyl ether (1.88 mL, 12 mmol) and triethylamine (3.63 mL, 36 mmol) in 30 mL of CH₂Cl₂ at 0 °C. The suspension was allowed to warm to rt and stirred overnight. Then the organic layer was washed with brine and sat. aq. NH₄Cl solution. The residue was purified by column chromatography (50 % ethyl acetate in hexane) to yield 4.5 g of the product as a white solid (72 % yield). ¹H-NMR (250 MHz, CDCl₃): δ 8.29(d, *J* = 1.8 Hz, 2 H, Ar-H), 8.20 (t, *J* = 1.8 Hz, 1 H, Ar-H), 4.44 (t, *J* = 5.1 Hz, 2 H, CO₂-CH₂), 3.79 (t, *J* = 5.1 Hz, 2 H, O-CH₂), 3.71-3.60 (m, 6 H, O-CH₂), 3.55-3.51 (m, 2 H, O-CH₂) 3.34 (s, 3 H, O-CH₃); ¹³C-NMR (125 MHz, CDCl₃): δ 163.54, 149.16, 137.68, 133.24, 94.27, 71.87, 70.59, 70.53, 68.92, 64.67, 58.95; FAB-MS (*m*-nitrobenzylalcohol (MNBA), 3 kV): *m/z* = 521.2 (calcd 521.1 for C₁₄H₁₉O₅I₂⁺), 543.1 (calcd 543.0 for C₁₄H₁₈O₅I₂Na⁺); Anal. C: 32.15, H: 3.13 (calcd C: 32.33, H: 3.49); HPLC (90 % MeOH / 10 % H₂O, 1 mL/min): 100.0 % peak area.

(2-Ethyl)-hexyl 3,5-diiodobenzoate (2a): Compound **B** (0.56 g, 1.5 mmol) was mixed with thionyl chloride (10 mL) and refluxed for 2 h. Excess thionyl chloride was removed *in vacuo* and the remaining residue was dried on a vacuum pump for 3 h to afford the crude acid chloride as a white solid. It was then added to a stirring solution of 2-ethyl-hexanol (0.19 mL, 1.5mmol) and triethylamine (0.62 mL, 4.5 mmol) in 10 mL of CH₂Cl₂ at 0 °C. The suspension was allowed to warm to rt and stirred overnight. Then the organic layer was washed with brine and sat. aq. NH₄Cl solution. The residue was purified by column chromatography (hexane) to yield 0.6 g of the product as colorless oil (82 % yield). ¹H-NMR (250 MHz, CDCl₃): δ 8.26(d, *J* = 1.5 Hz, 1 H, Ar-H), 8.19 (t, *J* = 1.5 Hz, 2 H, Ar-H), 4.20 (d, *J* = 1.5 Hz, 2 H, CO₂-CH₂), 1.74-1.64 (m, 1 H,

CH), 1.46-1.22 (m, 8 H, CH), 0.94-0.88 (m, 6 H, CH); ^{13}C -NMR (125 MHz, CDCl_3): δ 163.73, 149.02, 137.61, 94.31, 68.18, 38.78, 30.43, 28.90, 23.86, 22.87, 13.98, 10.95; EI-MS (80 eV, 100 °C): m/z = 486.0 (calcd 486.1 for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{I}_2^+$); HPLC (90% MeOH in H_2O , 1 mL/min): 99.37 % peak area.

(2-Ethyl)-hexyl 3-bromo-5-(3,3-diethyl-1-triazenyl)-benzoate (7a): Compound **C** (1.64 g, 5 mmol), potassium carbonate (0.13 g, 1 mmol) and 2-ethyl-hexanol (2.3 mL, 15 mmol) were suspended in DMF (15 mL) and heated overnight at 140 °C. The reaction mixture was poured into water and extracted with hexane followed by column chromatography (2 % ethyl acetate in hexane) to give 1.8 g of product as yellow oil (87 % yield). ^1H -NMR (250 MHz, CDCl_3): δ 7.94 (dd, J = 1.8 Hz, 1.8 Hz, 1 H, Ar-H), 7.84 (dd, J = 1.8 Hz, 1.8 Hz, 1 H, Ar-H), 7.71 (dd, J = 1.8, 1.8 Hz, 1 H, Ar-H), 4.15 (d, J = 5.4 Hz, 2H, $\text{CO}_2\text{-CH}_2$), 3.73 (q, J = 7.2 Hz, 4 H, NCH_2), 1.74-1.62 (m, 1 H, CH), 1.50-1.22 (m, 14 H, CH), 0.94-0.81 (m, 6 H, CH); ^{13}C -NMR (125 MHz, CDCl_3): δ 165.50, 152.61, 132.43, 128.21, 126.84, 122.41, 120.86, 67.60, 38.88, 30.51, 28.92, 23.93, 22.87, 13.90, 10.95; FAB-MS (MNBA, 3 kV): m/z = 412.1 (calcd 412.1 for $\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}_2\text{Br}^+$).

(2-Ethyl)-hexyl 3-(3,3-diethyl-1-triazenyl)-5-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (8a): Dry and degassed triethylamine (50 mL) was added to a mixture of compound **D** (4.94 g, 12 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.27 g, 0.24 mmol), CuI (0.04 g, 0.24 mmol), and PPh_3 (0.31 g, 1.2 mmol) followed by the addition of trimethylsilylacetylene (3.4 mL, 24 mmol). The flask was sealed and the solution was stirred overnight at 80 °C. The reaction mixture was diluted with diethylether, filtered, and concentrated leaving a red colored oil, which was purified by column chromatography (2 % ethyl acetate in hexane) to give 4.12 g of the product as a yellow oil (80 % yield). ^1H -NMR (250 MHz, CDCl_3): δ 7.98 (dd, J = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 7.83 (dd, J = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 7.66 (dd, J = 2.2 Hz, 1.5 Hz, 1 H, Ar-H), 4.21 (d, J = 5.8 Hz, 2 H, $\text{CO}_2\text{-CH}_2$), 3.73 (q, J = 7.3 Hz, 4 H, NCH_2), 1.75-1.66 (m, 1 H, CH), 1.48-1.23 (m, 14 H, CH), 0.94-0.88 (m, 6 H, CH), 0.23 (m, 9H, $\text{Si}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3): δ 165.90, 151.27, 131.20, 128.97, 127.46, 123.65, 121.87, 104.42, 94.21, 67.29, 38.82, 30.47, 28.88, 23.87, 22.85, 13.92, 10.95, -0.20; EI-MS (80 eV, 120 °C): m/z = 429.4 (calcd 429.2 for $\text{C}_{24}\text{H}_{39}\text{N}_3\text{O}_2\text{Si}^+$); Anal. C: 67.21, H: 9.26, N: 9.14 (calcd C: 67.09, H: 9.15, N: 9.78).

(2-Ethyl)-hexyl 3-iodo-5-[2-(1,1,1-trimethylsilyl)-1-ethynyl]-benzoate (1a): Compound **E** (1.16 g, 2.7 mmol) was dissolved in 15 mL of CH_3I , the reaction mixture was degassed and

refilled with argon three times then sealed and stirred at 110 °C for 16 h. The CH₃I was removed under reduced pressure and the brown colored residue was purified by column chromatography (2 % ethyl acetate in hexane) to give 0.85 g of the product as a light yellow oil (69 % yield). ¹H-NMR (250 MHz, CDCl₃): δ 8.25 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 8.01 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 7.95 (dd, *J* = 1.5 Hz, 1.5 Hz, 1 H, Ar-H), 4.21 (d, *J* = 5.8 Hz, 2 H, CO₂-CH₂), 1.75-1.65 (m, 1 H, CH), 1.48-1.23 (m, 8 H, CH), 0.94-0.80 (m, 6 H, CH), 0.23 (s, 9 H, Si(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃): δ 164.45, 144.21, 138.11, 132.0, 125.3, 102.0, 97.07, 93.03, 67.99, 38.80, 30.45, 28.90, 23.88, 22.87, 13.94, 10.93, -0.30; EI-MS (80 eV, 90 °C): *m/z* = 456.3 (calcd 456.1 for C₂₀H₂₉IO₂Si⁺), 441.2 (calcd 441.3 for C₁₉H₂₆IO₂Si⁺); Anal. C: 52.0, H: 6.30 (calcd C: 52.64, H: 6.40); HPLC (95 % MeOH / 5 % H₂O, 1 mL/min): 95.0 % peak area.

Polymer synthesis

General procedure for AB' polycondensation: The monomer (1 mmol), CuI (0.1 mmol) and the Pd(PPh₃)₄ (0.06 mmol) were loaded in a flame dried 10 mL Schlenk Tube, which was evacuated and refilled with argon. Dry and degassed benzene (for non-polar monomers **1a** and **2a**) or acetonitrile (for polar monomers **1b** and **2b**) (4 mL in each case) was submitted to the tube via a syringe, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 6 mmol) was added immediately followed by addition of distilled water (1-10 mmol depending on experiment, see manuscript: Table 1). The tube was covered with aluminum foil and the reaction mixture was allowed to stir at rt for 3 d. The reaction mixture was precipitated in 500 mL of methanol (for polymers **3a**) or diethyl ether (for polymers **3b**), the resulting solid was dissolved in CH₂Cl₂ and passed through a short silica column to give the desired polymer as light yellow colored solid.

General procedure for A₂+BB' polycondensation: The monomer (1 mmol), CuI (0.1 mmol), and Pd(PPh₃)₄ (0.06 mmol) were loaded in a flame dried 10 mL Schlenk Tube, which was evacuated and refilled with argon. Dry and degassed benzene (for non-polar monomers **1a** and **2a**) or acetonitrile (for polar monomers **1b** and **2b**) (4.3 mL in each case) was submitted to the tube via a syringe, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 6 mmol) and trimethylsilylacetylene (TMSA, 1 mmol) were added immediately followed by addition of distilled water (1 mmol). The tube was covered with aluminum foil and the reaction mixture was allowed to stir at rt for 3 d. The reaction mixture was precipitated in 500 mL of methanol (for polymers **3a**) or diethyl ether (for polymers **3b**), the resulting solid was dissolved in CH₂Cl₂ and passed through a short silica column to give the desired polymer as light yellow colored solid.

Microwave-assisted polycondensation: The same procedures as described above were followed however, instead of stirring at rt the sealed tube was kept in the microwave reactor (for reaction times and temperatures see manuscript: Table 1).

Polymer characterization

Polymer 3a: $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ 8.16 (broad s, 2 H, Ar-H), 7.89 (broad s, 1 H, Ar-H), 4.27 (broad s, 2 H, $\text{CO}_2\text{-CH}_2$), 1.73 (broad s, 1 H, CH), 1.33 (broad s, 8 H, CH), 0.91 (broad s, 6 H, CH), see also: Figure 2; $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.17, 149.46, 138.04, 134.12, 94.71, 68.62, 39.22, 30.87, 29.34, 24.29, 23.28, 14.39, 11.34; for GPC, see Table 1.; Anal. C: 74.26, H: 7.13 (calcd for $(\text{C}_{17}\text{H}_{20}\text{O}_2)_n$ C: 79.65, H: 7.86); IR (KBr): 3422, 2957, 2929, 2859, 1723, 1644, 1596, 1455, 1235, 1114 cm^{-1} ; UV/vis (CHCl_3 , 25 $^\circ\text{C}$) λ_{max} = 290 nm, see also Figure 5.

Polymer 3b: $^1\text{H-NMR}$ (250 MHz, CDCl_3): δ 8.20 (broad s, 2 H, Ar-H), 7.90 (broad s, 1 H, Ar-H), 4.52 (broad t, 2 H, $\text{CO}_2\text{-CH}_2$), 3.87 (broad t, 2 H, O- CH_2), 3.72 (broad m, 6 H, O- CH_2), 3.52 (broad t, 2 H, O- CH_2), 3.34 (broad s, 3 H, O- CH_3), see also: Figure 2; $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 165.05, 138.41, 132.91, 131.20, 123.70, 89.12, 72.00, 70.76, 70.74, 70.69, 69.15, 64.66, 59.05, see also: Figure 1; for GPC, see also: Table 1 and Figure 4; Anal. C: 65.27, H: 5.62 (calcd for $(\text{C}_{16}\text{H}_{18}\text{O}_5)_n$ C: 66.19, H: 6.25); IR (KBr): 3435, 2873, 1724, 1597, 1451, 1243, 1110, 1029 cm^{-1} , see also: Figure 3; UV/vis (CHCl_3 , 25 $^\circ\text{C}$) λ_{max} = 290, 304 (shoulder) nm, (CH_3CN , 25 $^\circ\text{C}$) λ_{max} = 282 nm, see also: Figure 5.

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