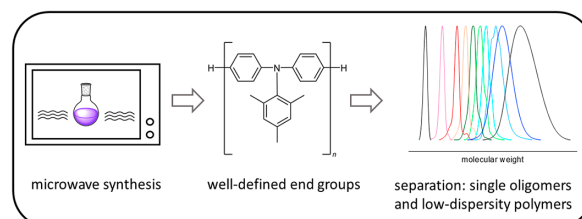


Microwave-Assisted Synthesis of Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) with Well-Defined End Groups and Narrow Dispersity

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Received: 07.06.2023

Accepted after revision: 27.07.2023

DOI: 10.1055/a-2145-4763; Art ID: OM-2023-06-0005-OA

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Abstract A series of PTAA (poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]) polymers were synthesized using a Ni(0)-mediated Yamamoto coupling. Polymers with different molecular weights and only one series of well-defined end groups were obtained with various amounts of a tailor-made endcapper. This level of structural uniformity has not yet been described for PTAA. By using microwave heating, it was possible to shorten the reaction time from at least 1 day to 30 min. The synthetic strategy allows the separation of single PTAA oligomers with up to 6 repeating units and polymer fractions with low dispersities from 1.06 to 1.17 by using preparative size exclusion chromatography. The carrier mobilities of the PTAA oligomers and polymers were derived from organic field-effect transistors. Mobilities increase with increasing molecular weight of the PTAA and are higher compared to commercially available PTAA samples.

Key words: PTAA, hole transport materials, microwave-assisted synthesis, preparative SEC, charge-carrier mobility

Introduction

Triarylamine is a common structural motif in charge-transporting materials.^{1–4} The most prominent example for polymeric triarylamine, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], commonly abbreviated as PTAA, is among the most frequently used hole transport materials (HTMs) in perovskite solar cells (PSCs).^{5,6} Originally developed for applications in organic field-effect transistors (OFETs)⁷, it was first applied to PSCs in 2013 by Noh et al.⁸ and Heo et al.⁹ and is a popular choice ever since because of its remarkable stability and good solubility in common organic solvents. Furthermore, some of the PSCs with the highest efficiencies use PTAA as HTMs.^{10,11}

PTAAs were originally synthesized by Veres et al.¹² via a reductive aryl–aryl coupling of dichlorotriarylamine monomers in the presence of nickel chloride and zinc. The molecular weights (MWs) were in the range of 3 kDa.^{4,12} Later, Zhang et al.¹³ obtained PTAAs via Suzuki cross-coupling, starting with a triphenylamine, asymmetrically substituted with a bromine and a boronate ester. Furthermore, the use of zerovalent bis(1,5-cyclooctadiene)nickel for the reductive coupling of dibromo monomers is often described for the synthesis of structurally related polymers.^{14–16} Depending on the reaction and catalyst system, the reaction may lead to a broad dispersity and different end groups. It has been shown that the MW and the dispersity can have a strong influence on the performance of organic solar cells¹⁷ or PSCs¹⁸ as these parameters affect the solubility, film formation, mechanical stability, morphology and in particular charge-carrier mobility. Meanwhile, PTAAs are commercially available from various suppliers. However, analytical parameters are not always fully provided by the supplier and batch-to-batch variability can still cause unexpected issues.¹⁹

In this paper, we present a microwave-assisted synthesis protocol to obtain well-defined PTAA polymers. In contrast to standard synthetic protocols, where reaction times vary from 1 to several days,^{12,13} our microwave-heated reactions proceeded smoothly and showed full conversion after only 30 min.^{20,21} By adding a monobrominated triphenylamine as an endcapper²² right from the beginning of the reaction, we ensured that all chains are terminated by a triphenylamine unit, leading to only one polymer-homologous series. By varying the amount of endcapper, we were able to access a wide range of MWs from 7 kDa up to 40 kDa. After polymerization, an oligomer-rich sample was further separated with a preparative size exclusion chromatography (SEC) set-up. By this, we obtained single oligomers (up to 6 repeating units) and several polymers with narrow dispersities between 1.06 and 1.17 in a single purification step. Such oligomers are interesting for two reasons: first, the physical properties of polymers can be predicted by extrapolation from the oligomers;^{23,24} second, we have used the oligomers to establish a SEC calibration which allows correction of the

SEC MWs obtained using a standard polystyrene calibration.²⁵

Results and Discussion

Screening of reaction parameters

Yamamoto polymerizations are considered difficult because of the oxygen- and moisture-sensitive nature of the Ni catalyst. When done in a conventional Schlenk tube using oil bath heating, two separate solutions of monomer and catalyst have to be prepared and separately degassed. After pre-heating the catalyst solution for approximately 30 min, the monomer solution is added and the reaction is heated for 24 h or even more. We envisioned a robust synthesis protocol that gives access to well-defined PTAA polymers for fundamental studies in a highly reproducible manner. As a starting point for our screening of reaction conditions, commercially available monomer **1** was polymerized with 5% 4-bromotriphenylamine (**2**) as an endcapper using Ni(COD)₂/COD/bipy (2,2'-bipyridine) as the catalyst system and heating the reaction in anhydrous DMF/toluene mixture for 24 h at 80 °C (Scheme 1).

While the polymer yield itself was satisfactory, the SEC curve (see Figure S3, Supporting Information) of the polymer displayed a shoulder indicating low-MW chains, which possibly arise from premature chain termination. We then investigated the influence of reaction parameters on the polymerization and the MW distribution of the polymers (Table 1).

A longer reaction time of 72 h (entry 2), as well as using 3 equiv of Ni(COD)₂/COD/bipy (entry 3) did not have a significant influence on the MW distribution. Also, lowering the temperature to 60 °C (entry 4) led to no improvement. Zhang et al.¹⁶ investigated the synthesis of polycarbazoles and reported that a different order of addition (adding the catalyst to the monomer solution) resulted in a significant increase of MW, presumably due to the formation of a different intermediate species, which is less prone to degradation. Unfortunately, in our case no positive effect was observed

Table 1 Molecular weights and dispersities for PTAA polymers **3** during the screening of reaction parameters

Entry	Deviation from standard conditions	$M_n^a/g \cdot mol^{-1}$	$M_w^a/g \cdot mol^{-1}$	D_M^a
1	–	6000	18000	3.00
2	72 h reaction time	5800	17000	2.95
3	3 equiv of catalyst reagents	5300	15000	2.85
4	60 °C	6100	18800	3.10
5	Different order of addition	4100	11900	2.91
6	Microwave heating 80 °C, 3 h	4200	11600	2.76
7	Microwave heating, 130 °C, 0.5 h	4600	15400	3.34
8	Entry 7, endcapper 7	6700	18800	2.80
9	Entry 8 in anhydrous THF	7000	17800	2.54

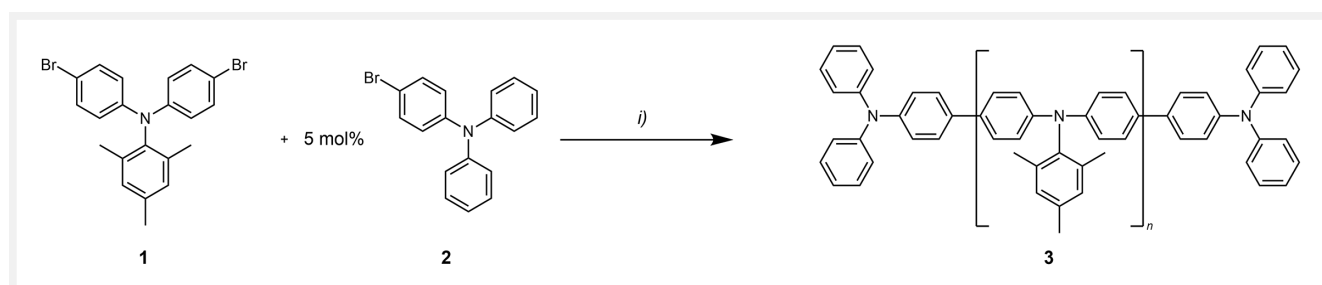
Standard reaction conditions: Ni(COD)₂ (2.0 equiv), COD (2.0 equiv), bipy (2.0 equiv), 4-bromotriphenylamine(**2**) (5 mol%) as endcapper, anhydrous DMF/toluene 24 h, 80 °C.

^a SEC measurement, polymer column with polystyrene calibration.

(entry 5). We then decided to try microwave heating, since microwave-assisted reactions are described to proceed significantly faster while reducing unwanted side reactions^{20,21,26} (entries 6 and 7). While obtaining similar MWs compared to the conventional heating, the handling of the reaction was improved significantly. All reagents could be added to the microwave vial under an inert atmosphere in a glove box. After the addition of the solvent, the vial was directly sealed, ensuring that no oxygen or moisture is present throughout the reaction. Without any further degassing or catalyst activation step, the polymerization was initiated by microwave heating. To ensure a maximum of structural similarity, 4-bromotriphenylamine (**2**) was replaced by endcapper **7**, which led to an increased MW. Changing the solvent to THF led to a narrowing of the dispersity to 2.54.

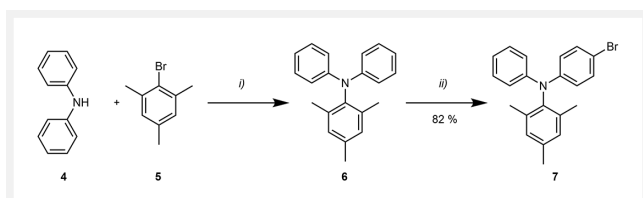
Synthesis of Endcapper **7**

During the course of the polymerization screening, it turned out necessary to have an endcapper with a maximum of structural similarity to the monomer. So, the mono-brominated repeating unit **7** was synthesized in two steps starting



Scheme 1 Yamamoto polymerization of monomer **1** and 4-bromotriphenylamine (**2**) to synthesize PTAA polymers of type **3**. i) Ni(COD)₂ (2.0 equiv), COD (2.0 equiv), bipy (2.0 equiv), 4-bromotriphenylamine (**2**) (5 mol%), anhydrous DMF/toluene 24 h, 80 °C.

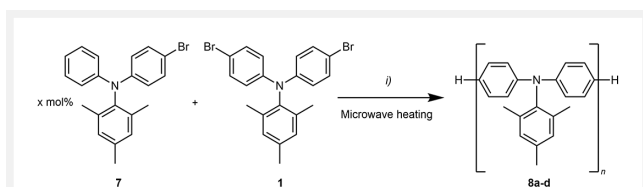
from commercially available diphenylamine (**4**) and mesityl bromide (**5**) (Scheme 2). By treating the intermediate **6** with exactly 1.0 equiv of *N*-bromosuccinimide (NBS), the desired product was obtained in good yield. Monobromination of aryl compounds is widely described in the literature and no double-brominated reaction product was formed, most likely because the second bromination occurs at a slower rate, since the monobrominated species is less electron-rich.^{27,28}



Scheme 2 Synthesis of the tailored endcapper **7**. i) Diphenylamine **4** (1.1 equiv), Pd(OAc)₂ (3 mol%), P(tBu)₃ (6 mol%), NaOtBu (1.4 equiv), toluene, 110 °C, 92% yield; ii) NBS (1.0 equiv), CHCl₃, ambient temperature, 82% yield.

Synthesis of Well-Defined PTAAAs

With the optimized endcapper structure and reaction conditions in hand, we synthesized a series of PTAAAs by polymerizing monomer **1** with different amounts of endcapper **7** (Scheme 3).

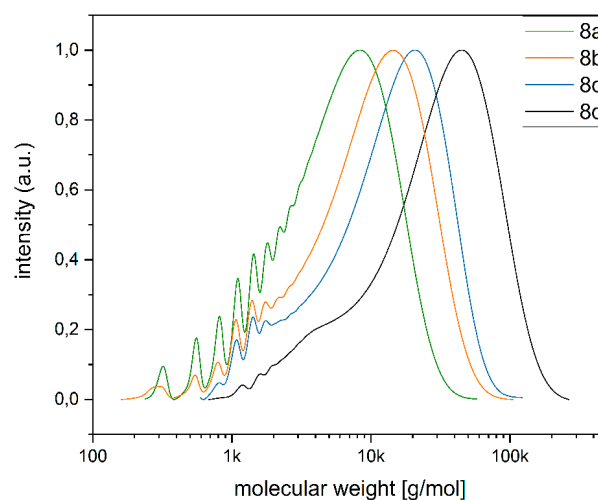


Scheme 3 Microwave-assisted synthesis of PTAA polymers **8a-d**. (i) Ni(COD)₂ (2.0 equiv), COD (2.0 equiv), 2,2'-bipyridine (2.0 equiv), anhydrous THF, 130 °C for 30 min.

The resulting polymers were analyzed by SEC. As expected, the addition of larger amounts of endcapper **7** leads to a decrease in MW from 40.8 kDa to 7.8 kDa (Table 2). In samples **8a-c** with lower MW, the signals of single oligomers can be observed.

Figure 1 shows the MALDI-ToF spectra of PTAA **8a** (green) and PTAA **8c** (blue), indicating that the endcapping process was successful, because only one homologous series is present in both polymers. The peak distance of 286 Da corresponds well to the MW of one repeating unit. To the best of our knowledge, the presence of only one series of end groups in PTAA has not been reported. Usually, more than one set of end groups is present, as can be seen in the spectrum of a

Table 2 Normalized SEC chromatograms and molecular weights and dispersities for PTAAAs **8a-d** synthesized with different amounts of endcapper



Sample	Endcapper mol%	M_n^a /g · mol ⁻¹	M_w^a /g · mol ⁻¹	\mathcal{D}_M^a
8a	20	3600	7800	2.17
8b	10	4650	13 100	2.82
8c	5	7000	17 800	2.54
8d	2.5	14 050	40 800	2.90

^a SEC measurement, polymer column with polystyrene calibration.

commercial PTAA sample (see Figure S4, Supporting Information). The peak MW of sample **8a** is about 1500 Da. Sample **8c** with a lower amount of endcapper has a peak MW at about 2000 Da. We will come back to MW determination later, when we discuss the separation of monodisperse oligomers.

PTAA **8a** with only one homologous series and a large amount of oligomers appears suitable for separation of single oligomers using a preparative SEC setup in recycle mode. In recycle mode, the sample passes a three-way valve after elution, where it either can be collected or passes the column set for another time, leading to an increased column length and a better separation without adding extra columns and pressure increase. The recycle mode is especially powerful for the separation of single oligomers.^{23,29,30}

In Figure 2, the elution diagram of the preparative SEC with polymer **8a** in recycle mode is shown.

Even during the first run, details of oligomeric species are clearly visible. With increasing run number, the signals get broader and more details become visible. This also means that the polymer part would slowly overtake the oligomers of the previous run and signals would run into each other. To prevent this, it turned out necessary to remove the polymer parts rather early (**8a-10** was collected in the second run and **8a-9** in the third run). With the oligomer signals becom-

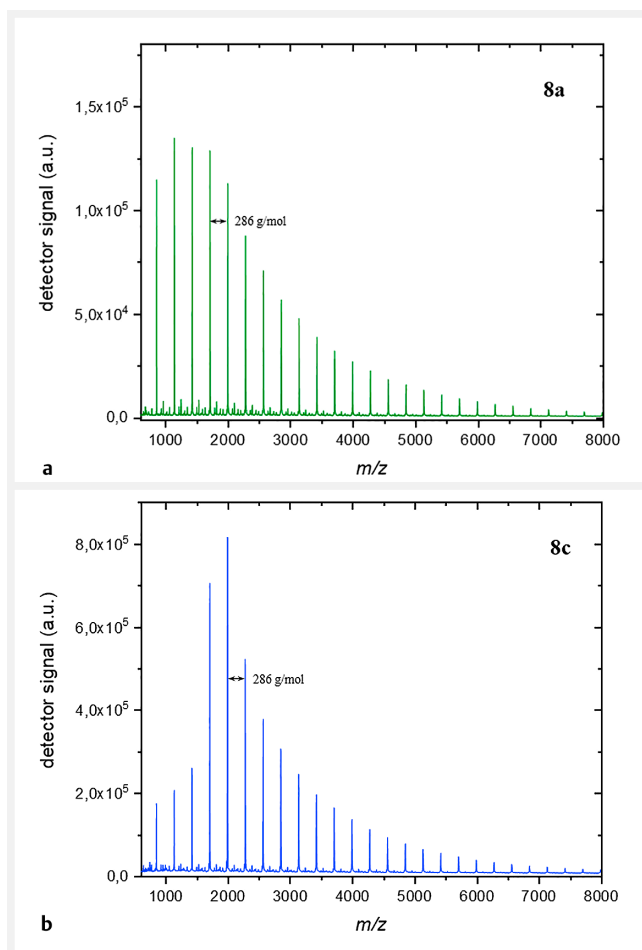


Figure 1 MALDI-ToF spectra of PTAA **8a** (green) and PTAA **8c** (blue).

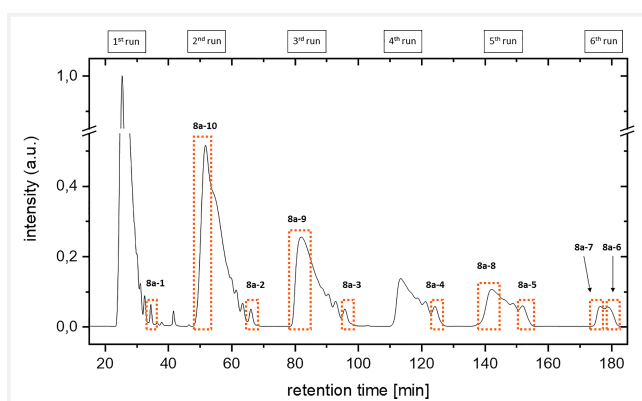


Figure 2 Preparative SEC elution diagram of 80 mg **8a** in recycle mode. The orange boxes indicate the collection of the respective fraction.

ing more pronounced, the last distinct signal of each run was also collected. By doing so, the dimer (**8a-1**) was collected right in the first run, while the trimer (**8a-2**) and tetramer (**8a-3**) were obtained in runs two and three, respectively. Overall, 80 mg of crude polymer was separated into 10 fractions. Analytical SEC scans of each fraction are shown in Figure 3 and the respective values for M_n and M_w are summarized in Table 3.

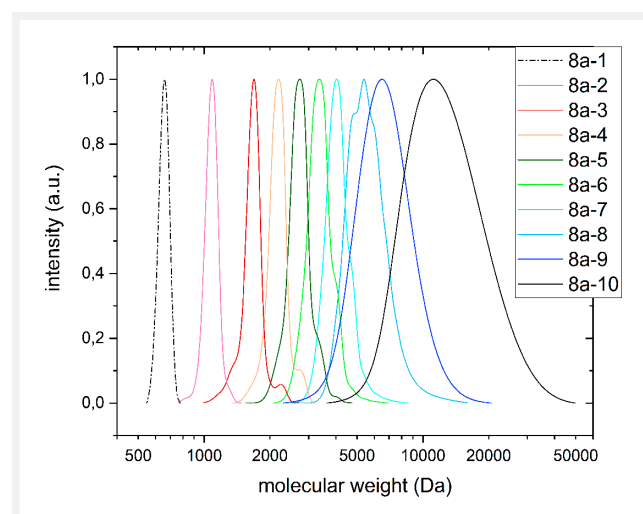


Figure 3 Normalized SEC chromatograms for PTAA fractions **8a-1** – **8a-10** separated with SEC in recycle mode (calibrated with polystyrene). Fractions **8a-1**–**8a-8** were measured with an oligomer SEC setup; polymeric fractions **8a-9** and **8a-10** were measured using polymer SEC (see the Supporting Information for column details).

Table 3 Molecular weights and dispersities for PTAA fractions **8a-1** – **8a-10** separated with SEC in recycle mode

Fraction		$M_n^a/\text{g}\cdot\text{mol}^{-1}$	$M_w^a/\text{g}\cdot\text{mol}^{-1}$	\mathcal{D}_M^a
8a-1	Dimer	653	655	1.003
8a-2	Trimer	1075	1081	1.006
8a-3	Tetramer	1648	1671	1.01
8a-4	Pentamer	2153	2179	1.01
8a-5	Hexamer	2699	2741	1.01
8a-6	Oligomer ^b	3349	3412	1.02
8a-7	Oligomer ^b	4048	4125	1.02
8a-8	Oligomer ^b	5450	5700	1.06
8a-9	Polymer ^c	6400	6950	1.08
8a-10	Polymer ^c	11660	13600	1.17

^a Analytical SEC measurement with polystyrene calibration. ^b Oligomer fraction with low dispersity. ^c Polymer fraction with low dispersity.

It is clearly visible from the SEC curves and the dispersity value below 1.01 that fractions **8a-1** and **8a-2** only contain one discrete oligomer. This can also be seen in the MALDI-ToF spectra of the respective fractions (Figure 4), with only the dimer peak at $m/z = 572$ visible for fraction **8a-1** and the peak of the trimer at $m/z = 858$ in fraction **8a-2**. The curves of fractions **8a-3–8a-6** display a small shoulder, which corresponds to the respective $n + 1$ oligomer. For example, fraction **8a-4** mostly consists of the pentamer ($m/z = 1428$), but also contains a notable amount of hexamer ($m/z = 1713$). The fractions **8a-5** and **8a-6** show small signals from both the $n - 1$ and the $n + 1$ oligomers. In addition to discrete, single oligomers, fractions **8a-8–8a-10** contain polymers covering a range from 5000 up to 13 600 Da with very narrow dispersities of 1.06 to 1.17.

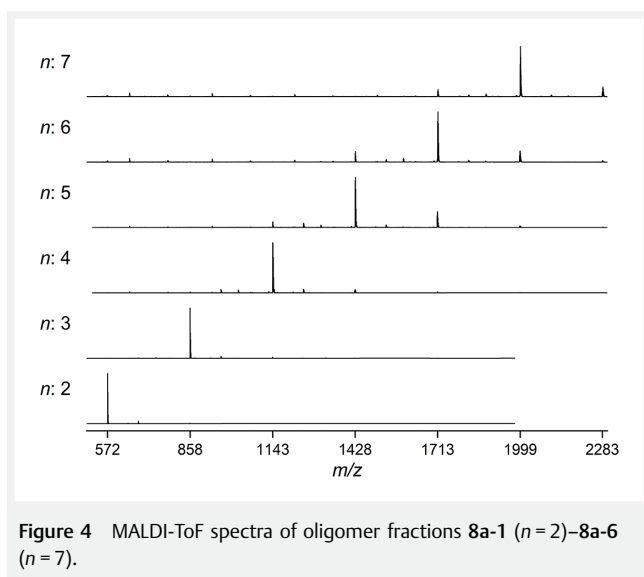


Figure 4 MALDI-ToF spectra of oligomer fractions **8a-1** ($n = 2$)–**8a-6** ($n = 7$).

When comparing the MWs of fractions **8a-1–8a-7** determined by MALDI-ToF measurements with the values obtained from SEC, one can see that the polystyrene calibration overestimates the MW. Since we know the exact MWs of these fractions, we set up a calibration curve for these oligomers ranging from 2 to 8 repeating units. Figure 5 shows both the polystyrene calibration and the calibration curve derived from the PTAA oligomers from the dimer ($n = 2$, MW = 572 Da) up to the octamer ($n = 8$, MW = 2283 Da). It can be observed that for the dimer, the MALDI and polystyrene calibration are almost identical. The deviation becomes more pronounced with increasing chain length. For the octamer, which has a MW of 2283 Da, the calculated MW derived from the polystyrene calibration would be approximately 4100 Da, which gives an overestimation by a factor of almost 2. This effect can be explained by the rigid aromatic backbone of PTAA. With increasing chain length, the PTAA chains are stiffer than polystyrene

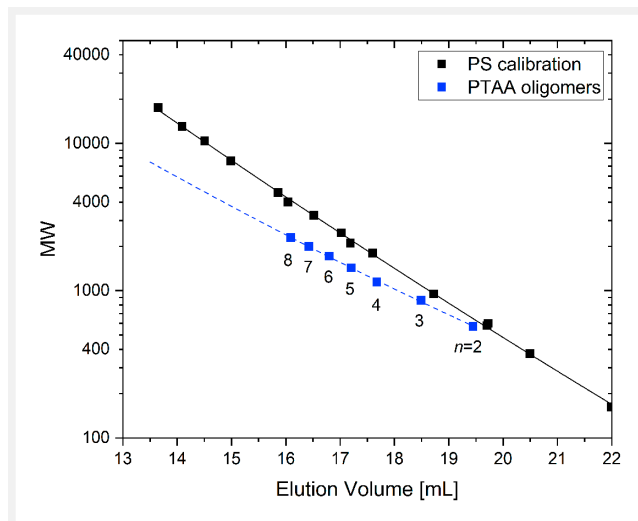


Figure 5 PTAA oligomer (blue) and polystyrene (black) calibration curves; the lines correspond to the 2nd-order polynomial fits of the experimental data points; the numbers indicate the PTAA repeating units.

with the same MW and therefore have a higher hydrodynamic radius, which causes an overestimation when using polystyrene standards.

With one single separation step, we were able to collect 10 different PTAA fractions ranging from single oligomers to narrowly distributed polymers, covering a range from 572 g/mol for the dimer **8a-1** up to 11 000 g/mol for polymer **8a-10**. This would not have been possible with other post-synthesis treatments, like fractionated Soxhlet extractions, which clearly shows the capability of our preparative SEC approach.

Charge-Carrier mobilities

Bottom gate/bottom contact OFETs were fabricated from selected polymer samples, to investigate the relationship between chain length and charge-carrier mobility, while also comparing our polymers to commercially available PTAA samples.

We chose fractions **8a-4** (pentamer), **8a-6** (heptamer) and the two polymeric samples **8a-9** ($M_n = 6410$ g/mol) and **8a-10** ($M_n = 11 660$ g/mol), as well as two commercial polymers **A2** ($M_n = 10 640$ g/mol) and **A3** ($M_n = 5610$ g/mol). The respective polymers were spun-cast from chlorobenzene solution on commercially available OFET substrates and mobilities were calculated by plotting the square root of the drain current I_d versus the gate voltage V_g (see the Supporting Information for details). The polymer characteristics as well as calculated charge-carrier mobilities are summarized in Table 4. All polymer samples formed amorphous films and showed no signs of crystallization.

Table 4 Polymer characteristics and charge-carrier mobilities of PTAA samples calculated from OFET transfer curves

Fraction	$M_n^a/g \cdot mol^{-1}$	$M_w^a/g \cdot mol^{-1}$	D_M^a	$\mu [cm^2 \cdot V^{-1} \cdot s^{-1}]$
8a-4	2150	2180	1.01	4.0×10^{-5}
8a-6	3350	3410	1.02	3.4×10^{-4}
8a-9	6400	6950	1.08	3.3×10^{-3}
8a-10	11660	13600	1.17	2.7×10^{-3}
A2	10640	35450	3.3	9.4×10^{-4}
A3	5610	9160	1.6	1.5×10^{-3}

^a SEC measurement with polystyrene calibration.

As expected, the pentamer **8a-4** displayed the lowest mobility with $4.0 \times 10^{-5} cm^2 \cdot V^{-1} \cdot s^{-1}$, which is increased by 1 order of magnitude with the addition of two repeating units (heptamer **8a-6**) to $3.4 \times 10^{-4} cm^2 \cdot V^{-1} \cdot s^{-1}$. Going to longer chains led to a further increase in mobility up to $3.3 \times 10^{-3} cm^2 \cdot V^{-1} \cdot s^{-1}$ for polymer **8a-9** (~20 repeating units), whereas the longest polymer **8a-10** (~40 repeating units) shows a similar mobility of $2.7 \times 10^{-3} cm^2 \cdot V^{-1} \cdot s^{-1}$. It is noteworthy that the polymers **8a-9** and **8a-10** outperformed the two commercial polymers **A2** and **A3**, which have a similar M_n , but a much broader dispersity, as well as nonuniform end groups. This indicates that narrow dispersities and well-defined end groups are beneficial for device performance. Figure 6 shows the obtained mobilities plotted against the MW of the respective PTAA fraction.

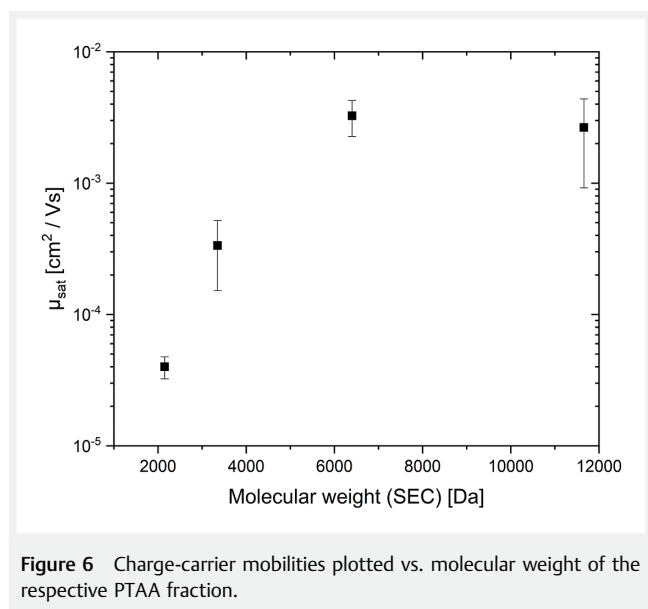


Figure 6 Charge-carrier mobilities plotted vs. molecular weight of the respective PTAA fraction.

Overall, these values are among the best values published for PTAA. Veres et al.³¹ reported mobilities in the range of $2-5 \times 10^{-3} cm^2 \cdot V^{-1} \cdot s^{-1}$. Zhang et al.¹³ obtained $4 \times 10^{-3} cm^2 \cdot V^{-1} \cdot s^{-1}$ for a PTAA with $M_n = 46500 g/mol$ and

a dispersity of 2.11. However, in both references, the OFETs have been optimized, e.g. various device architectures as well as dielectrics and gate insulators have been tested.³¹

Conclusions

We have demonstrated a new microwave-assisted synthesis to obtain PTAA with well-defined MWs and a high structural uniformity with only one series of end groups. With the help of microwave heating, we were able to decrease reaction times to only 30 min for full conversion, while the same reaction would take 24 h or longer to complete using conventional heating techniques.

The high structural uniformity allowed us to separate a crude polymer into several single oligomers (dimer up to hexamer) as well as polymeric fractions in a range from ~5000 up to 11600 g/mol with narrow dispersities of 1.06 to 1.17, using a preparative SEC setup. It is noteworthy that all these fractions were accessible from one batch of starting material without further synthetic work in one single separation. This clearly shows the capability of preparative SEC compared to other separation techniques for oligomers and polymers.

Furthermore, we tested a series of four PTAA in a range from 5 to approximately 40 repeating units, as well as two commercially available polymers in OFETs to determine the charge-carrier mobility. Increasing the chain length from oligomers to ~20 repeating units leads to an increase in mobility by almost 2 orders of magnitude from 4.0×10^{-5} to 3.3×10^{-3} , so a certain chain length is beneficial for a high mobility. Overall, the mobilities for our polymers are higher compared to two commercially available samples and are among the best values published for PTAA.^{7,13,31}

Microwave synthesis and separation through preparative SEC are broadly applicable techniques that are suitable for a wide range of polymers. Combining both is a powerful toolbox that gives rapid access to polymers with narrow MW distribution and even single, discrete oligomers. These model substances are valuable for fundamental studies, as the properties of defect-free polymers can be predicted from a series of monodisperse oligomers.

Experimental Section

All air-sensitive reactions were carried out under argon as an inert gas in flame-dried glassware. NiCOD₂ was purchased from Sigma Aldrich. COD, 2,2'-bipyridine, NBS, mesityl bromide, THF, CHCl₃ and toluene were purchased from Acros, N,N-bis(4-bromophenyl)-2,4,6-trimethylaniline and NaOtBu from TCI, and diphenylamine from abcr. All reagents were used as received without further purification.

Analytical thin-layer chromatography (TLC) was performed on Polygram SIL G/UV sheets by Macherey-Nagel. The visualization of TLC plate was performed by UV (254 nm).

Flash column chromatography was performed using normal phase silica gel 60 (63–200 μm). All mixed solvent eluents are reported as v/v solutions.

^1H and ^{13}C NMR spectra were taken in deuterated chloroform (CDCl_3 , purchased from Sigma Aldrich) using a Bruker Avance 300 (300 MHz) spectrometer. The CHCl_3 residual peak (7.26 ppm for ^1H and 77.16 ppm for ^{13}C) was used for calibration.

Microwave reactions were performed with a Biotage Initiator+ system. The accessories (vials, caps, stirring bars, etc.) were also purchased from Biotage and were used as received.

The preparative SEC was performed on a Shimadzu LC-20AP HPLC separation module with a Shimadzu SPD-20A UV detector eluting with unstabilized THF. The column set and the pre-column were purchased from Agilent. Two columns are the PLgel 100 \AA (20×300 mm, $10 \mu\text{m}$, up to $5000 \text{ g} \cdot \text{mol}^{-1}$) and one PLgel 500 \AA (20×300 mm, $10 \mu\text{m}$, 500 – $25000 \text{ g} \cdot \text{mol}^{-1}$) and one PLgel MIXED-D (20×300 mm, $10 \mu\text{m}$, 200 – $400000 \text{ g} \cdot \text{mol}^{-1}$).

The analytical SEC was performed on a Waters system with a Waters 2998 UV detector eluting with unstabilized THF. Weight-average MWs and number-average MWs were calculated relative to linear polystyrene standards.

MALDI-ToF-MS spectra were taken with a Bruker Autoflex max spectrometer. DCTB or dithranol were used as matrix materials.

Procedures

Screening of Reaction Parameters (Table 1)

General Procedure for Yamamoto Polymerization without Microwave Heating

A flame-dried Schlenk flask was charged with $\text{Ni}(\text{COD})_2$ (247 mg, 0.898 mmol, 2.0 equiv), 2,2'-bipyridine (bipy) (140 mg, 0.898 mmol, 2.0 equiv) and COD (91 mg, 0.898 mmol, 2.0 equiv). After the addition of anhydrous DMF (5 mL), the resulting purple solution was degassed by three consecutive pump-freeze-thaw cycles and then heated at 60°C for 30 min. Meanwhile, monomer **1** (200 mg, 0.449 mmol, 1.0 equiv) and 4-bromotriphenylamine (**2**) (7.3 mg, 0.00225 mmol, 0.05 equiv) were dissolved in anhydrous toluene (10 mL) in a separate Schlenk flask and the solution was degassed by three consecutive pump-freeze-thaw cycles. After the 30 min, the monomer solution was transferred to the catalyst solution via a syringe and the reaction was stirred for 24 h at 80°C . Afterwards, the reaction mixture was poured into 100 mL of MeOH/conc. hy-

drochloric acid (1 : 1) and stirred for 1 h. The green solution was extracted with CHCl_3 (3×100 mL) and the combined organic phases were washed with alkaline EDTA solution (5 wt %, set to pH 8–9 with aq. NH_3) to remove Ni residues and then dried with MgSO_4 . The solvent was removed on a rotary evaporator. After column chromatography (Alox N, THF), the polymers were obtained as a yellow solids.

Table 1, Entry 1:

This reaction was carried out exactly according to the general procedure described above.

Yield: 131 mg (97%), polymer SEC: M_n : 6000 Da, M_w : 18000 Da, Đ_M : 3.00.

Table 1, Entry 2:

This reaction was carried out according to the general procedure, but was heated for 72 h instead of 24 h.

Yield: 120 mg (89%), polymer SEC: M_n : 5800 Da, M_w : 17000 Da, Đ_M : 2.95.

Table 1, Entry 3:

This reaction was carried out using the following amounts: $\text{Ni}(\text{COD})_2$ (371 mg, 1.35 mmol, 3.00 equiv), COD (146 mg, 1.35 mmol, 3.00 equiv), 2,2'-bipyridine (210 mg, 1.35 mmol, 3.00 equiv).

Yield: 110 mg (81%), polymer SEC: M_n : 5300 Da, M_w : 15000 Da, Đ_M : 2.85.

Table 1, Entry 4:

This reaction was carried out according to the general procedure, but was heated at 60°C instead of 80°C .

Yield: 110 mg (81%), polymer SEC: M_n : 6100 Da, M_w : 18800 Da, Đ_M : 3.10.

Table 1, Entry 5:

This reaction was carried out according to the general procedure, but after heating the catalyst solution (in 10 mL of anhydrous DMF) for 30 min, it was transferred into the degassed monomer solution.

Yield: 111 mg (82%), polymer SEC: M_n : 4100 Da, M_w : 11900 Da, Đ_M : 2.91.

Table 1, Entry 6:

A microwave vial was charged with monomer **1** (200 mg, 0.449 mmol, 1.0 equiv), 4-bromotriphenylamine (**2**) (7.3 mg, 0.00225 mmol, 0.05 equiv) and 2,2'-bipyridine (bipy) (140 mg, 0.898 mmol, 2.0 equiv) and was then transferred into a nitrogen-filled glovebox. In the glovebox, $\text{Ni}(\text{COD})_2$ (247 mg, 0.898 mmol, 2.0 equiv) and COD (91 mg, 0.898 mmol, 2.0 equiv) and 5 mL of dry DMF and 10 mL of toluene were added and the vial was sealed. After microwave irradiation at 80°C for 3 h, the reaction mixture was poured into 100 mL of MeOH/conc. hydrochloric acid (1 : 1) and stirred for 1 h. The green solution was extracted with

CHCl₃ (3 × 100 mL) and the combined organic phases were washed with alkaline EDTA solution (5 wt%, set to pH 8–9 with aq. NH₃) to remove Ni residues and then dried with MgSO₄. The solvent was removed on a rotary evaporator. After column chromatography (Alox N, THF), the polymer was obtained as a yellow solid.

Yield: 55 mg (43%), polymer SEC: M_n : 4200 Da, M_w : 11 600 Da, \overline{M}_w : 2.76.

Note: the low yield compared to other reactions was due to a broken beaker during the workup.

Table 1, Entry 7:

This reaction was carried out like entry 6, but it was microwave-irradiated at 130 °C for 30 min.

Yield: 114 mg (85%), polymer GPC: M_n : 4600 Da, M_w : 15 400 Da, \overline{M}_w : 3.34.

Table 1, Entry 8:

This reaction was carried out like entry 7, but with endcapper **7** (8.3 mg, 0.00225 mmol, 0.05 equiv).

Yield: 122 mg (90%), polymer SEC: M_n : 6700 Da, M_w : 18 800 Da, \overline{M}_w : 2.81.

Table 1, Entry 9:

This reaction is described under PTAA **8c** (Table 2).

Synthesis of Endcapper 7

1. 2,4,6-Trimethyl-*N,N*-diphenylaniline (**6**)

In a flame-dried Schlenk flask, 2-bromo mesitylene (**5**) (1.99 g, 10.0 mmol, 1.0 equiv), diphenylamine (**4**) (1.86 g, 11.0 mmol, 1.10 equiv), NaOtBu (1.34 g, 14.0 mmol, 1.40 equiv) and Pd(OAc)₂ (0.067 g, 0.30 mmol, 0.03 equiv) were dissolved in 25 mL of dry toluene. Next, P(*t*Bu)₃ (1 M solution in toluene, 600 μL, 0.60 mmol, 0.06 equiv) was added and the resulting dark-red solution was stirred at 110 °C overnight. After cooling, the reaction was quenched with H₂O and the mixture was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were dried with MgSO₄ and the solvent was removed on the rotary evaporator. The title compound was obtained after flash column chromatography (silica, hexane/CH₂Cl₂ 7:1 → 4:1) as a white solid.

Yield: 2.65 g (9.24 mmol, 92%).

¹H NMR (CDCl₃, 300 MHz): δ = 7.24–7.15 (m, 4 H), 7.02–6.92 (m, 6 H), 6.92–6.84 (m, 2 H) 2.34 (s, 3 H), 2.00 (s, 6 H) ppm.

The NMR data we obtained were in good agreement to those reported in the literature.³²

2. *N*-(4-Bromophenyl)-2,4,6-trimethyl-*N*-phenylaniline (**7**)

NBS (1.24 g, 6.94 mmol, 1.0 equiv) was slowly added to a stirred solution of triarylamine **6** (2.00 g, 6.94 mmol, 1.0 equiv) in CHCl₃ (35 mL). After 3 h, the solution was diluted

with CHCl₃ to approximately 100 mL and filtered over a silica plug (approx. 3 × 5 cm), before the solvent was removed on a rotary evaporator. After flash column chromatography (silica, hexane/CH₂Cl₂ 95:5), the title compound was obtained as a white solid.

Yield: 2.08 g (5.68 mmol, 82%).

¹H NMR (CDCl₃, 300 MHz): δ = 7.35–7.16 (m, 4 H), 7.06–6.81 (m, 7 H), 2.36 (s, 3 H), 2.02 (s, 6 H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ = 145.6, 145.4, 139.7, 137.6, 137.2, 132.0, 130.1, 129.3, 121.4, 120.8, 120.0, 112.4, 21.2, 18.6 ppm.

MS (EI pos.): *m/z* = 367, 365 (both [M]⁺)

Synthesis of PTAA 8a–d by Yamamoto Coupling

A microwave vial was charged with monomer **1** (200 mg, 0.449 mmol, 1.0 equiv), endcapper **7** (2.5–20 mol%) and 2,2'-bipyridine (bipy) (140 mg, 0.898 mmol, 2.0 equiv) and was then transferred into a nitrogen-filled glovebox. In the glovebox, Ni(COD)₂ (247 mg, 0.898 mmol, 2.0 equiv) and COD (91 mg, 0.898 mmol, 2.0 equiv) and 5 mL of dry THF were added and the vial was sealed. After microwave irradiation at 130 °C for 30 min, the reaction mixture was diluted with 5 mL of THF and poured into 100 mL of MeOH/conc. hydrochloric acid (1:1) and stirred for 1 h. The green solution was extracted with CHCl₃ (3 × 100 mL) and the combined organic phases were washed with alkaline EDTA solution (5 wt %, set to pH 8–9 with aq. NH₃) to remove Ni residues and then dried with MgSO₄. The solvent was removed on a rotary evaporator. After column chromatography (Alox N, THF), the polymers were obtained as a yellow solid (70–92%).

In the case of PTAA **8d** (with 2.5% endcapper), the crude polymer was further subjected to Soxhlet extraction with acetone for 24 h and the residue was used for further studies.

PTAA 8a (Table 2):

Yield: 140 mg (90%), polymer SEC: M_n : 3600 Da, M_w : 7800 Da, \overline{M}_w : 2.17.

PTAA 8b (Table 2):

Yield: 143 mg (92%), polymer SEC: M_n : 4650 Da, M_w : 13 100 Da, \overline{M}_w : 2.82.

PTAA 8c (Table 2):

This reaction was carried out with the following amounts: monomer **1** (400 mg, 0.898 mmol, 1.00 equiv), endcapper **7** (16.5 mg, 0.0449 mmol, 0.05 equiv), 2,2'-bipyridine (280 mg, 1.796 mmol, 2.00 equiv), Ni(COD)₂ (494 mg, 1.796 mmol, 2.00 equiv), COD (192 mg, 1.796 mmol, 2.00 equiv), anhydrous THF (10 mL).

Yield: 180 mg (70%), polymer SEC: M_n : 7000 Da, M_w : 17 800 Da, \overline{M}_w : 2.54.

PTAA 8d (Table 2):

Yield: 90 mg (70%), polymer SEC: M_n : 14050 Da, M_w : 40800 Da, \bar{M}_n : 2.90.

Funding Information

We gratefully acknowledge financial support from the Bavarian State Ministry of Education, Science and the Arts through the Collaborative Research Network “Solar Technologies go Hybrid” (SolTech). Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 491183248 – and by the Open Access Publishing Fund of the University of Bayreuth.

Acknowledgment

The authors thank Adrian Hochgesang for his help with the OFET measurements and device preparation and Dr. Sven Hüttner for fruitful discussions.

Supporting Information

Supporting Information for this article is available online at <https://doi.org/10.1055/a-2145-4763>.

Conflict of Interest

The authors declare no conflict of interest.

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