Polymer Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Polymer Chemistry

Paper

Robust procedure for large scale synthesis of a high molar mass, unsubstituted poly(*m*,*p*-phenylene)†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bernd Deffner and A. Dieter Schlüter*

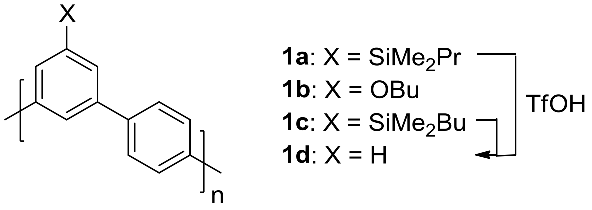
Due to the absence of functional groups and the relative inertness of phenylene units, polyphenylenes are an interesting research target for materials such as films and fibers, combining some π-π conjugation with chemical (e.g. hydrolytic) and thermal robustness. However, unsubstituted polyphenylenes can practically not be obtained at high molar masses due to their poor solubility already at an early stage of growth. Herein, we report a synthetic route which nevertheless provides such polymers in a two-step process recently promoted by Sakamoto et al. First, a soluble precursor poly(*m*,*p*-phenylene) is obtained by AA/BB-type Suzuki polycondensation (SPC) which is then subjected to a virtually quantitative removal of its solubilizing side chains. SPC was carried out on a multigram scale using highly pure monomers which resulted in a fully reproducible and scalable route that provided up to 14 g of a substituted poly(*m*,*p*-phenylene) with a molar mass of 150 kg mol^{-1} (300 kg mol^{-1} after removal of the common cyclic side products). This molar mass is amongst the highest ever reported in the open literature for SPC. The precursor polymer was compression moulded into films which were then subjected to side chain cleaving conditions by simple immersion into acidic solutions. Gratifyingly, the side chains could almost completely be removed with preservation of the overall film shape. We consider this work a step towards novel stiff and strong fluorescing films and fibers resistent to hydrolytic conditions.

Introduction

Polyphenylenes have been on the radar of materials science for several decades.[1–8] Initially, electrical conductivity of these polymeric materials in their oxidized form was in the focus. This focus then slowly shifted towards optoelectronic applications in e.g. organic light emitting diodes or photovoltaics[9–12], as well as towards high performance materials.[13–16] This development, which was supported by an industrial engagement, was possible because of the discovery of Suzuki polycondensation (SPC) in the late 1980s.[17] SPC, which is based on the famous Suzuki-Miyaura cross-coupling reaction (SMCC),[18,19] provided for the first time access to aromatic polymers whose aromatic entities are directly connected to one another via C-C bonds and not through ester, amide or imide linkages.[6] An important feature of SPC is its regioselectivity. Coupling between aromatic units occurs exclusively at the carbon atoms which carry the functional groups (typically boronic esters and halides) required for bringing about SMCC. This was the key to the all-straight, exclusively *para*-linked poly(*para*-phenylene)s (PPP) as well as to the kinked poly(*meta*-phenylene)s[20,21] and in principle also to poly(*ortho*-phenylene)s[22] supposed the appropriate monomers are being employed. Because of the conformationally rather restricted nature of all these polymers, synthesis of high molar mass products requires measures to keep the growing chains in solution until the required chain length is reached. This is commonly achieved by the attachment of flexible side chains to the monomers, which improve solubility of the resulting polymer for entropic reasons and less favourable crystallisation.[23,24] This is why unsubstituted high molar mass polyphenylenes are practically unknown, with a recent work by Sakamoto et al. based on the transformation of the poly(*meta*-*para*-phenylene) (P*mp*P) **1a** into the parent polymer **1d** being a noticeable exception.[25] A cleaving concept was applied, in which flexible chains serve as an auxiliary and are removed after polymerisation. This concept uses acid-cleavable silyl groups and has also been applied in related cases by other authors.[26–28] While decoration with flexible side chains is enormously useful whenever solubility of a target polymer is an issue, side chains also have a downside: Not only do they dilute the intrinsic backbone properties but they can also detrimentally affect the stability of polymers towards thermal and chemical impact.

Laboratory of Polymer Chemistry, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.

† Electronic Supplementary Information (ESI) available: Synthesis of catalyst Pd[$PPh_2C_6H_5CO_2H$]$_3$. ^1H and ^{13}C solution NMR spectra of monomers, ligand **L2** and polymer **1c**. Gas chromatograms of **2** at different concentrations. Full TGA curves, DSC curves, IR spectra and ^{13}C-CP/MAS solid state NMR spectra of polymer **1c** before and after treatment with TfOH. See DOI: 10.1039/x0xx00000x



Scheme 1. Chemical structure of the three substituted poly(*para-meta*-phenylene) (P*mp*P) **1a**-**1c** and the unsubstituted P*mp*P **1d** which is the target polymer of the present study.

Side chains are best be viewed as carry-on solvent or carry-on plasticizer for the backbone, and it is therefore common understanding that e.g. the mechanical properties such as stiffness and strength of substituted polyphenylenes are inferior to the hypothetical parent polymers.[29] In a recent publication, it was shown that the P*mp*P **1b** with flexible butyloxy side chains has a considerable Young's modulus of 1 GPa and rivals the toughness of commercially available amorphous polycarbonate.[20] Given this interesting finding, it was of obvious attraction to investigate whether this polymer can be accessed in the unsubstituted form; this had already been the goal of the mentioned work on polymer **1a**.[25] Based on our experience, we expected unsubstituted polyphenylenes such as **1d** to exhibit interesting mechanical properties for molar masses exceeding approximately 100 kg mol^{-1}. Unfortunately, we could not even get close to this molar mass range with polymer **1a,** presumably because the growing chains started to precipitate at molar masses of 35-40 kg mol^{-1}. In the present study we therefore report on polymer **1c,** the silyl side chain of which differs from **1a** by just one methylene unit. On the one hand this seemingly small structural variation is a compromise between the need to improve the solubility and on the other hand the wish to add as little mass as possible to the side chains because they have to be removed later on anyway. Removal of large mass fractions of a polymeric material processed into a fiber or a film can cause severe mechanical destruction and render the final product practically worthless despite the fact that the chemistry may have proceeded perfectly well.

Here we report on 1, 3, 10 and 18 g-scale polymerisations to starting polymer **1c**, which is obtained in a fully reproducible fashion of up to a 9 g polymer (after removal of cyclic byproducts). Because of the high monomer purity and the large polymerisation scale, the molar masses are reproducible in the range of 150 kg mol^{-1}, which is believed to be close to what SPC can offer in this case. The polymers are then subjected to side chain cleavage both when in solution and in hot compression moulded films of approximately 0.05 – 0.6 mm thickness. Removal of the chains is investigated by thermogravimetric analysis (TGA) as well as by IR- and MAS solid-state ^{13}C NMR spectroscopy both in terms of kinetics and conversion.

Experimental section

Materials

All reagents were purchased from ABCR, Acros, Aldrich, Apollo Scientific or TCI and used without further purification. Dry solvents were distilled using a solvent drying system from LC Technology Solutions Inc. SP-105 under nitrogen atmosphere (H2O content <10 ppm as determined by Karl-Fischer titration). All reaction vessels were dried in an oven at 80°C overnight. For moisture sensitive reactions the flasks were additionally dried under vacuum with a heat gun. Pd[P(*p*-tolyl)$_3$]$_3$ (Pd(**L1**)$_3$) was freshly prepared following the literature procedure[30] and stored in a glove-box under N_2 at room temperature. The ligand 4-(diphenylphosphino)benzoic acid (**L2)** was synthesised according to the literature procedure.[31] The corresponding catalyst Pd[PPh$_2$C$_6$H$_5$COOH]$_3$ (Pd(**L2**)$_3$) was synthesised according to the procedure in the supporting information. 1,4-Benzenediboronic acid bis(pinacol) ester (**3**) was synthesized and purified following the published procedure.[32]

Characterisation

Solution NMR spectra were recorded on a Bruker AVANCE (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometer at room temperature using deuterated chloroform (CDCl$_3$) or dimethyl sulfoxide (DMSO-d$_6$). The solvent signal was used as an internal standard for the chemical shift (^{1}H: $\delta = 7.26$ ppm, ^{13}C: $\delta = 77.00$ ppm for chloroform and ^{1}H: $\delta = 2.50$ ppm, ^{13}C: $\delta = 39.50$ ppm for DMSO). High resolution mass spectrometry (HRMS) was performed by the MS-service of the Laboratory for Organic Chemistry at ETH Zürich using ESI-FTICR-MS (Bruker solariX) and EI-Sector-MS (Waters Micromass AutoSpec Ultima). Analytical GPC measurements were performed using a Viscotek GPC-system with chloroform as eluent, equipped with a pump and a degasser (GPCmax VE2001, flow rate 1.0 ml min^{-1}), a detector module (Viscotek 302 TDA), a UV detector (Viscotek 2500, $\lambda = 54$ nm) and two columns (1 × PLGel Mix-B and 1 × PLGel Mix-C, 7.5×300 mm for each). Conventional calibration was performed with polystyrene standards (Polymer Laboratories) in the range of M_p 1480 to 4340000 g mol^{-1}. Prior to injection, the sample solution was filtered through a sintered stainless steel filter (pore size 2 µm). TGA analyses were performed under air with a TA Instruments Q500 thermogravimetric analyser (heating rate: 20 °C min^{-1}).

Synthesis of (3,5-dibromophenyl)butyl(dimethyl)silane (2)

In a dry 6 L three-neck flask 1,3,5-tribromobenzene (44.52 g, 0.141 mol) was dissolved in 3 L of dry diethyl ether. The mixture was cooled to -78°C with an acetone dry ice bath and a 1.6 M hexane solution of *n*-butyl lithium (88.93 mL, 0.141 mol) was added dropwise. The reaction was stirred for 2 h at -78°C and then *n*-butylchlorodimethylsilane (21.32 g, 0.141 mol) was slowly added. The mixture was heated to room temperature overnight, quenched with water (300 mL) and diluted with diethyl ether (300 mL). The organic phase was separated and washed with water (300 mL) and brine

(300 mL). The combined aqueous phases were extracted with diethyl ether and the combined organic phases were dried over magnesium sulphate, followed by solvent removal. The residual brown liquid was pre-purified by a short silica column which led to a bright yellow liquid. Distillation at 165 °C and 0.1 mbar gave the product as colourless viscous oil. In order to achieve the desired purity the distillation was repeated twice (40.23 g, 81.2%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.64 (t, *J* = 1.8 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 2H), 1.32 (m, 4H), 0.90 (t, *J* = 1.8 Hz, 3H), 0.76 (m, 2H), 0.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.3, 134.6, 123.2, 26.4, 25.8, 15.0, 13.7, -3.2; HRMS (EI) m/z: $[M]^+$ calcd. for $C_{12}H_{18}Br_2Si$, 347.9539; found, 347.9539. Analysis calcd. for $C_{12}H_{18}Br_2Si$: C, 41.16; H, 5.18; Si, 8.02; Br, 45.64. Found: C, 40.97; H, 5.38; Br, 45.85.

Typical procedure for Suzuki polycondensation (1c)

In a 1 L Schlenk flask, a precise amount of the dibromo monomer **2** (10.028 g, 28.639 mmol) and 1.005 eq. of the diboron monomer **3** (9.499 g, 28.782 mmol) were dissolved in a mixture of THF (600 mL) and water (200 mL). 25 mL saturated K_2CO_3 (aq.) were added and the biphasic system was degassed by applying five vacuum and nitrogen back-filling cycles. The catalyst Pd(**L2**)$_3$ (88.10 mg, 85.93 µmol) was dissolved in THF, which has prior been degassed by three freeze-pump-thaw cycles. The catalyst suspension was added under nitrogen counter flow and the resulting mixture was heated to 85°C for 48 h, during which time a colourless precipitate formed. The reaction was quenched with 150 mL toluene and 100 mL water. As soon as the solid was dissolved, the phases were separated and the organic phase was washed with 200 mL of saturated $NaHCO_3$ (aq.). To remove residual Pd, the organic phase was washed with a solution of 40 mg NaCN dissolved in 100 mL water by vigorous stirring of the biphasic mixture for 3 h. The phases were again separated and the organic phase was washed twice with 100 mL of saturated $NaHCO_3$ (aq.) followed by solvent removal. The residue was dissolved in 70 mL of toluene and the product was precipitated by dropping this solution in 700 mL of methanol. After filtration the colourless polymer was dried in vacuum at 75°C. (7.30 g, 96%) ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.90 (s, 1H), 7.80 (m, 6H), 1.40 (m, 4H), 0.90 (m, 5H), 0.38 (s, 6H); 13C NMR (75 MHz, $CDCl_3$, δ): 141.4, 140.8, 140.8, 133.3, 133.0, 131.6, 129.2, 128.4, 128.0, 126.8, 26.7, 26.3, 15.6, 14.0, -2.7. Analysis calculated for $C_{18}H_{22}Si$: C, 81.14; H, 8.32; Si, 10.54. Found: C, 81.31; H, 8.27.

Removal of cyclic byproducts

The raw polymer **1c** was placed in a Soxhlet apparatus and extracted with hot acetone for 5 d. During the extraction, the partially soluble macrocycles precipitated in the solvent reservoir. The polymeric material was dried and re-dissolved in toluene (0.1 g mL^{-1}). By dropwise addition of this solution into acetone (10-fold volume) the linear polymer was precipitated as a colourless solid. After filtration the material was dried in vacuum for 3 d at 75 °C.

Film preparation

800 mg of the purified and fractionated polymer were dissolved in 7.20 g of chloroform (10% w/w). The viscous solution was filtered into a petri dish (Ø 9 cm) through a plug of glass wool inside a pipette. The dish was covered and the solution dried at room temperature over 4 d. Thereafter, water was added, which helped lifting the film from the glass dish. The film was removed from the water surface and dried under vacuum at 75 °C for 5 d and subsequently hot compression moulded at 220 °C and 0.6 MPa pressure. The resulting films were approximately 100 µm thick. For thicker films, either the amount of polymer or the diameter of the petri dish were adjusted.

Side chain cleavage using dissolved 1c

Polymer **1c** was dissolved in 15 mL of toluene and heated to 110 °C. After 2 h, TfOH (2 mL) was added dropwise, which led to the precipitation of a brownish powder. The mixture was kept at 110 °C for 1 h, then cooled to room temperature, followed by the addition of NEt_3 (2 mL). Upon addition of methanol (10 mL), the solid was filtered off and washed with toluene. Polymer **1d** was yielded as a brownish solid (30 mg, 53%).

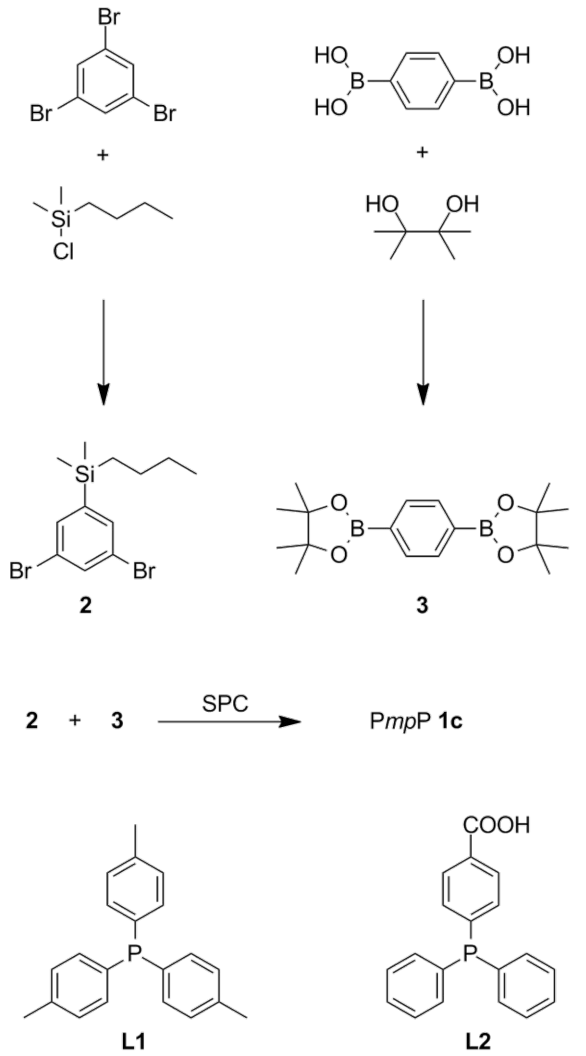
Side chain cleavage using a film of 1c

A 10 wt.% solution of TfOH in toluene was prepared in a glass vial and the polymer film was immersed within. After the desired time (1, 10, 60 min), the film was transferred into another glass vial containing a 10 wt.% NEt_3 solution in toluene. After 12 h, the film was transferred into another vial with pure toluene, where it was kept for 2 h to remove residual NEt_3. Finally, the sample was placed on a glass dish and dried first at 75 °C and ambient pressure for 12 h, followed by 5 d at 75 °C under vacuum.

Results and discussion

Monomer & Polymer Synthesis

From the beginning, we were aiming at a scalable and cost efficient process and therefore focused on an AA/BB approach of Suzuki polycondensation, which avoids the often tedious desymmetrisation of monomers required for the alternative AB approach.[33,34] 3,5-Dibromo (butyldimethylsilyl)benzene (**2**) and 1,4-benzenediboronic acid bis(pinacol) ester (**3**) were therefore used as monomers. They were synthesised on multi gram scales (**2**: 40 g; **3**: 50 g) following a straightforward protocol starting from commercial compounds (Scheme 2). The crude products **2** and **3** were purified by vacuum distillation using a Vigreux column and by recrystallisation from diethylether, respectively. Their purities were analyzed using samples from the monomer batches which served as stock for the series polymerisations. They were consistently found to exceed 99.5% by NMR spectroscopy (for **2** and **3**) and gas chromatography (for **2**). For details, see ESI. Additionally, both compounds gave correct values for elemental analysis.



Scheme 2. Synthesis of monomers **2** and **3** and their polymerisation to P*mp*P **1c** using a Pd-catalyst stabilised with the phosphine-based ligands **L1** and **L2**.

A large number of polymerisations were carried out, only a meaningful selection of which is presented here and collected in Table 1.

The first experiments aimed at finding out whether the by one methylene unit extended cleavable substituent would have an impact on the outcome. The conditions were applied as reported [0.6 mol-% of Pd(**L1**)$_3$]^{35} and the reactions were carried out on the 1 g scale. A representative result, listed as entry 1 in Table 1, shows that the molar mass range remained practically the same (≈35 kg mol^{-1}). This value refers to a raw GPC elution curve still containing cyclic oligomers. Also, the ratio of cyclic to linear products (approximately 30:70 based on mass recovery) was similar. We refrain from describing this aspect in greater detail because the ratio of cyclic to linear products was not given in Ref. 25 and therefore had to be crudely estimated from a GPC elution curve provided in this reference`s SI. Interestingly though, the polymers stayed in solution, while in the reported case they precipitated, which indicates an increased solubility of **1c** compared to **1a** and therefore a potential for higher molar masses. By stepwise increasing the monomer concentration in order to disfavor cycle formation similar weight averages for the molar masses were obtained. While in fact the ratio of cycles in the product could be reduced (as judged by GPC; Figure 1a), the molar mass of the linear material somewhat decreased (Table 1, entries 2-4). It was thus concluded that the reactivity of the reported catalyst based on the tris(*p*-tolyl)phosphine ligand may not have been sufficiently high, leading to premature termination. Consequently, the new catalyst precursor Pd(**L2**)$_3$ was used, for which Cheng et al.^{31} reported a particularly high reactivity. This Pd-complex carries the phosphine ligand **L2** (Scheme 2) mediating water solubility.

First experiments using this catalyst were performed without implementing other changes, and the results are condensed into entry 6. As can be seen, a significant increase in molecular weight was observed (55 kg mol^{-1}). A direct comparison of both catalysts, Pd(**L1**)$_3$ and Pd(**L2**)$_3$, supported this finding (Figure S16). That this improved reactivity was in fact due to the change in catalyst and not the change in base (K_2CO_3 instead of $NaHCO_3$) can be concluded from entry 5, where only the base was changed but not the catalyst. The molar mass obtained in this case was even lower than in the previous entries. While the increased molar mass with the new conditions (Pd(**L2**)$_3$ /K_2CO_3) was attractive, the fraction of cyclic products had not decreased much (GPC). At this point, the options were to either try to suppress the inherent problem with cycle formation of kinked monomers in step-growth polymerisations^{36,37} or to rather ignore this aspect and work on improving the molar mass of the linear product further and rely on an efficient separation protocol of cyclic and linear products. We opted for the latter and looked particularly into stoichiometry and scale (for other optimisation studies, see Refs. 38-40).

It is routine in SPC to use the boronic acid ester component in slight excess to meet the required 1:1 stoichiometry despite eventual deboronation reactions.^{38} Typically 1.02-1.03 equivalents are employed.^{39,40} In the present study, in a series of optimisation experiments, the following monomer ratios were employed: **3**:**2** = 1.000, 1.004, 1.005, 1.006, 1.007, and 1.008. The highest molar mass was observed for 1.005 (see Figure S17 and Table S1) which was found for three independent monomer batches. This ratio was therefore considered reliable and used for all following experiments. Next, the scale of the polymerisation was gradually increased from 1 g (entry 6), to 3 g (entry 7), 10 g (entry 8) and, finally, 18 g (entry 9). Note that this scale refers to the quantity of monomer **2**, which happens to have virtually the same molar mass as monomer **3**. The polymerisations were therefore carried out with 6 g, 20 g and 36 g of monomers. Interestingly, the corresponding raw molar masses increased continuously (Table 1). In all these experiments the concentration of freshly (!) prepared, brightly yellow catalyst precursor Pd(**L2**)$_3$ was kept at 0.3 mol-%. The products of entries 8 and 9 were subjected to a work-up procedure consisting of the two-step Soxhlet extraction with acetone and fractionating precipitation. This allowed the removal of a large fraction of the cyclic byproducts. A MALDI-TOF spectrum of the removed

Table 1. Conditions and results of the Suzuki polycondensation protocol applied to monomers **2** and **3** (ratio 1:1.05) with purities exceeding 99.5%. GPC molar masses refer to raw samples (except for entries marked by α and β) using conventional calibration with polystyrene standard.

Entry	Catalyst	Conc. [g/L]	Base	M_n [kg*mol^{-1}]	M_w [kg*mol^{-1}]	Yield [%]	P*mp*P **1c** [g]
1	Pd(**L1**)$_3$	12	NaHCO$_3$	5.0	35	85	0.7
2	Pd(**L1**)$_3$	18	NaHCO$_3$	4.4	32	83	0.6
3	Pd(**L1**)$_3$	24	NaHCO$_3$	6.2	27	80	0.6
4	Pd(**L1**)$_3$	36	NaHCO$_3$	8.8	32	75	0.5
5	Pd(**L1**)$_3$	12	K$_2$CO$_3$	5.2	17	88	0. 7
6	Pd(**L2**)$_3$	12	K$_2$CO$_3$	6.0	55	84	0.7
7	Pd(**L2**)$_3$	12	K$_2$CO$_3$	9.3	88	94	2.2
7a$^{\alpha,\beta}$				41	142	-	-
8	Pd(**L2**)$_3$	12	K$_2$CO$_3$	9.3	101	96	7.3
8a$^{\alpha}$				29	142	73	5.6
8b$^{\beta}$				42	147	53	4.1
9	Pd(**L2**)$_3$	12	K$_2$CO$_3$	8.0	151	99	14.3
9a$^{\alpha}$				25	277	76	10.9
9b$^{\beta}$				46	304	64	9.2

$^{\alpha}$ After Soxhlet extraction with acetone. $^{\beta}$After precipitating into acetone.

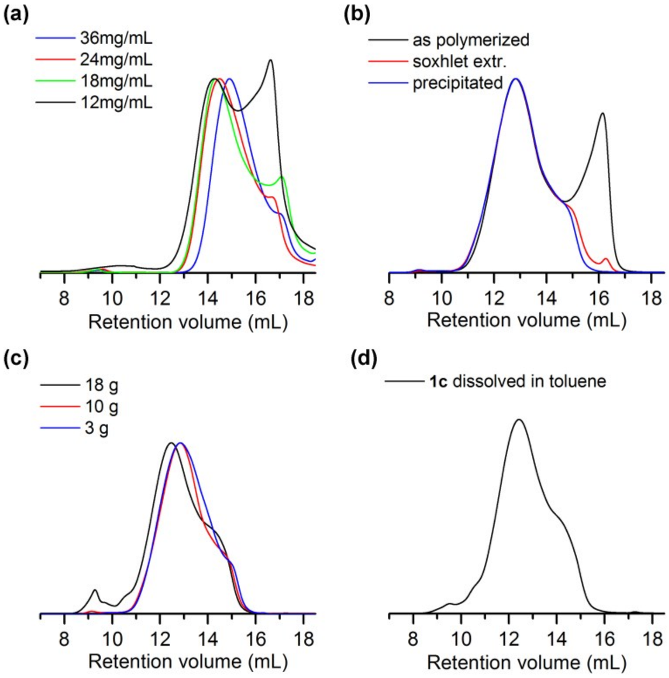


Figure 1. GPC elution curves of polymers P*mp*P. (a) As obtained from experiments performed at different concentrations (Table 1, entries 1-4), (b) after applying purification procedures aiming at removal of cyclic by-products, (c) as obtained from experiments performed at different scales (3, 10, 18 g of monomer **2**) and after cycle removal (blue: entry 7a ; red: entry 8c; black: entry 9c), and (d) as obtained from the 18 g experiment in (c) after prolonged dissolution in toluene at 38 °C prior to GPC analysis to reduce the aggregates appearing at extremely short elution times.

fraction shows the predominant macrocycle content (Figure S23). The impact of each of these steps on molar mass and recovered polymer mass is provided in Table 1 in entries 8a,b and 9a,b respectively, and can also be assessed from Figure 1b. While abandoning the second purification step is attractive for time reasons, it is recommended to nevertheless perform both steps if highest quality material is needed. The T_g values of polymers **1c** lie between 173 and 183 °C, which is an interesting range for applications at elevated temperatures (for DSC curves, see Figure S22). As can be seen from entries 6 - 9, very substantial improvements in terms of molar mass could be achieved. With each scale-up, the molar masses increased until the point when employing 18 g of monomer **2** led to a sixfold increase of the molar mass of polymer **1c** compared to entry 6 using only 1 g! Such masses are truly outstanding and underline the potential of SPC. While such optimisation series are more often disregarded than not, they are the fundament to evaluate whether just some result has been obtained or the best possible. Although an overestimation of molar mass for rigid polymers is observed when using GPC analysis with PS calibration[41], it is the most common method used. An in-depth determination is in progress. We note that all these experiments were performed with monomers from different batches. Thus, once high monomer purity is reached, it is the scale of the polymerisation that matters and thus, the stoichiometry! As can be seen from Figure 1c, the molar masses were so high that aggregates formed which did not easily dissolve upon extended shaking of the solutions prior to GPC analysis. The representative elution curve shown in Figure 1c exhibits a peak at very low retention times. That this peak is in fact due to aggregates can be shown by comparison with Figure 1d, which was obtained after prolonged shaking in 38 °C warm toluene. We suspect that the shoulder of the elution curve in 1d at low molar masses is due to residual cyclic products. The molar masses of this largest scale product **1c** were so high that the purification procedures mentioned above would have to be optimized again. The ^{1}H- and ^{13}C-NMR spectra of P*mp*P **1c** are well resolved and exhibit just the expected signals (Figures S8 and S9). At the end of this synthetic part, it is noted that there is a mass loss associated with the polymerisation. Not only are heavy functional groups (in particular bromine) lost in the course of SPC, but also the removal of cycles reduces the product mass by approximately 30%.

Side chain cleavage

The intention of this project was to provide reliable access to unsubstituted and high molar mass poly(*m,p*-phenylene) **1d**. After the completed synthesis and structure analysis of its precursor **1c**, we turned our attention to the removal of the side chains. Two different experiments were carried out using material from entry 7a (Table 1). For the first experiment, polymer **1c** was completely dissolved in boiling toluene and then exposed to TfOH and for the second, the polymer was hot compression moulded into films of different thicknesses, which were then exposed to the same acid. Both experiments relied on the same analytical methods which were TGA after exhaustive oxidation of all Si content into SiO_2, IR-spectroscopy, and ^{13}C-CP/MAS NMR spectroscopy. While the latter two methods are common praxis, TGA had to be validated first. For this purpose, the starting polymer **1c** was subjected to TGA with full access of air. Supposed full oxidation of all Si-content to SiO_2 takes place, the atomic ratio Si:C:H in **1c** would suggests a residual mass of 22.5% solely due to SiO_2. The experimentally observed value was 21.3% (Figure S18) which, taking into account the accuracy of TGA,[42] was considered good enough to apply the method. Additionally, it was confirmed by IR spectroscopy that the residue of the TGA experiments was in fact SiO_2. The solution cleaving experiment was conducted to create a reference point because post-polymerisation modifications in bulk are always confronted with a potentially hindered diffusion of reagents into the material. Upon acid addition to a solution of polymer **1c**, immediate precipitation of a brownish material was observed. Quantitative removal of the side chains was confirmed by subjecting the material to TGA analysis under ambient condition: at 600 °C, a mass loss of approximately 99% was observed (Figure S18). Having this benchmark, films of **1c** with thicknesses ranging from 0.05 - 0.6 mm were prepared by compression moulding at 220 °C. They were exposed in non-supported form to 10 % TfOH in toluene for times ranging from 10 sec to 60 min. Thereafter, the films were placed in a 10 wt-% NEt_3 solution in toluene for 12 h, and then washed and dried at 75 °C under vacuum. A few general observations shall be mentioned: a) with increasing exposure time to acid, the films appear darker; b) while all films remain largely in their initial form, the treatment causes slight crumpling (Figure 3); c) thicker films (≥0.3 mm) show pronounced swelling.

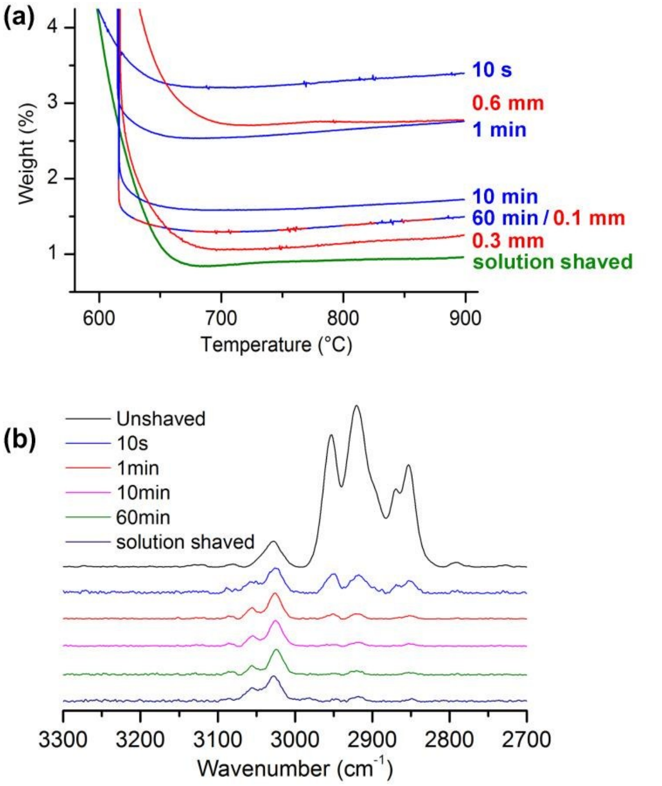


Figure 2: a) Magnification of TGA curves of different films after the cleaving procedure. The time series (blue) shows a decrease of the residual mass levelling off after 10 min of exposure to acid. The thickness series (red) showing an increase in residual mass with increasing film thickness. b) IR-spectra of the C-H stretching region proving the rapid progress of the cleaving reaction.

The TGA curves for all films are collected in Figure S18. The common feature is a dramatic mass loss at around 600 °C. Differences regard the exact point at which the loss sets in and how exactly it proceeds. Residual masses are in the very low percent range (Figure S18). In Figure 2a the blue curves refer to the dependence of residual mass on time of acid exposure for the same film thickness (0.1 mm) and the red curves to the dependence of residual mass on film thickness for the same acid exposure time (60 min). As can be seen, for the blue series the maximum effect is reached already within the first 10 min. More complete removal requires significantly increased exposure times. The red series shows that differences in film thickness from 0.1 mm to 0.6 mm cause differences in residual mass on the order of 1-2%, with the thinner films furnishing the better results. Given the accuracy of the method, which was estimated to be on the order of ±3%[42], we refrain from interpreting the finding in the sense that the result for the 0.3 mm film appears to be better than that for the 0.1 mm. While there is an evident impact of the cleaving conditions, the effects are subtle and the overall behaviour is similar: already after 10 sec of exposure time most of the side chains are removed. As the comparison with the material treated in solution shows (green line in Figure 2a), using the starting polymer in film form seems to be somewhat inferior. The findings based on TGA were corroborated by IR- and NMR spectroscopy. Figure 2b shows the high-frequency range of the

Figure 3: Compression moulded film with a thickness of 0.6 mm before exposure to acid (left) and after treatment with TfOH for 60 min (right). Besides the considerable shrinkage the overall shape of the film is largely retained while the transparency vanishes.

IR spectra of selected samples, where one can see the disappearance of the alkyl-CH-signals ($2810 < \tilde{\nu} < 2990$ cm^{-1}) while the aromatic CH-signals remain, though in altered form, reflecting the change in substitution pattern. The full TGA curves and IR spectra are provided in Figures S18 and S21, respectively. Figure S20 compares the ^{13}C-CP/MAS NMR spectra of starting material **1c** (entry 8b, Table 1) and product **1d** recorded from a 0.1 mm film that was treated with TfOH for 60 min. Figure 3 refers to a 0.6 mm thick film before (left) and after (right) side chain cleavage. After drying the acid-treated film, shrinkage is observed besides the vanishing transparency. Mechanically this film is stiffer but exhibits somewhat higher brittleness which shows when trying to bend by 180 °.

Conclusion

We have synthesised a soluble poly(*m,p*-phenylene) with a molecular weight of 150 kg mol^{-1} in a scale of 14 g. This polymer bears acid-cleavable side chains and was thus investigated for its potential to be converted into the parent polymer by acid treatment. Before subjecting the material to acidic conditions, the low molecular weight macrocyclic side products were removed to a large degree by Soxhlet extraction and subsequent precipitation. The fractionated polymer had a molecular weight of up to 300 kg mol^{-1} and was still available on the 9 g scale. It was processed into films of thicknesses between 0.1 and 0.6 mm by hot compression moulding. These films were then subjected to an acid treatment and the degree of side chain cleavage was determined by TGA, IR- and ^{13}C-CP/MAS solid state NMR spectroscopy. The removal occurs on a time scale of seconds and virtually complete removal was observed after maximally 60 min. Despite the mass loss associated with the side chain removal, films subjected to this process remained largely in shape. To the best of our knowledge, this is the first time an unsubstituted polyphenylene was obtained in film form, which is of obvious interest for applications.

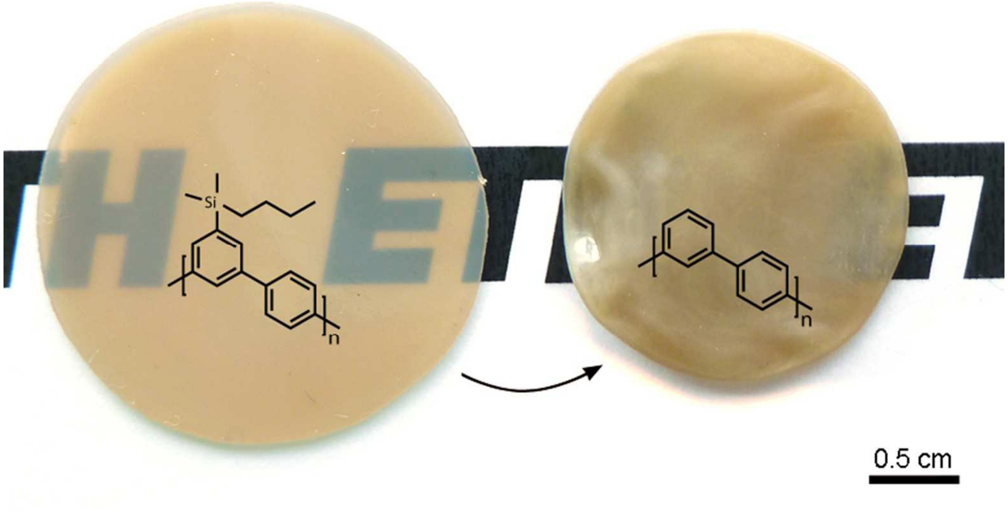
Acknowledgements

We cordially thank Dr. S. Jakob for help in the initial phase of this project, Dr. R. Verel, ETHZ, for recording the ^{13}C-CP/MAS NMR spectra, the group of Prof. P. Smith for access to microscopes and the hot press, and the group of Prof. J. A. van Bokhoven, ETHZ, for access to the gas chromatograph. Some of the GPC measurements were conducted in the group of Prof. M. Morbidelli, ETHZ. We also thank the mass spectrometry and elemental analysis services of the LOC, ETHZ, for their kind support. This work was financially supported by the Swiss National Science Foundation which is gratefully acknowledged.

Notes and references

1 J. M. Tour, *Adv. Mater.*, 1994, **6**, 190–198.
2 U. Scherf, *Top. Curr. Chem.*, 1999, **201**, 163–222.
3 A. C. Grimsdale and K. Müllen, *Angew. Chemie Int. Ed.*, 2005, **44**, 5592–629.
4 A. C. Grimsdale and K. Müllen, *Adv. Polym. Sci.*, 2006, **199**, 1–82.
5 A. C. Grimsdale and K. Müllen, *Adv. Polym. Sci.*, 2008, **212**, 1–48.
6 J. Sakamoto, M. Rehahn, G. Wegner and A. D. Schlüter, *Macromol. Rapid Commun.*, 2009, **30**, 653–687.
7 J. L. Brédas and R. Silbey, *Conjugated polymers: The novel science and technology of highly conducting and nonlinear optically active materials*, Kluwer Academic Publishers, Dordrecht, 1991.
8 M. Leclerc and J.-F. Morin, *Design and Synthesis of Conjugated Polymers*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010.
9 K. Müllen and U. Scherf, *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005.
10 C. Brabec, U. Scherf and V. Dyakonov, *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2014.
11 D. A. Bernards, G. G. Malliaras and R. M. Owens, *Organic Semiconductors in Sensor Applications*, Springer, Berlin Heidelberg, Germany, 2008.
12 A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897–1091.
13 K. Friedrich, T. Burkhart, A. A. Almajid and F. Haupert, *Int. J. Polym. Mater.*, 2010, **59**, 680–692.
14 D. Dean, M. Husband and M. Trimmer, *J. Polym. Sci. Part B Polym. Phys.*, 1998, **36**, 2971–2979.
15 C. P. Frick, A. L. Dirienzo, A. J. Hoyt, D. L. Safranski, M. Saed, E. J. Losty and C. M. Yakacki, *J. Biomed. Mater. Res. A*, 2013.
16 A. Almajid, K. Friedrich, A. Noll and L. Gyurova, *Plast. Rubber Compos.*, 2014, **43**, 138–144.
17 M. Rehahn, A.-D. Schlüter, G. Wegner and W. J. Feast, *Polymer (Guildf).*, 1989, **30**, 1060–1062.
18 A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147–168.
19 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457–2483.
20 R. Kandre, K. Feldman, H. E. H. Meijer, P. Smith and A. D. Schlüter, *Angew. Chemie Int. Ed.*, 2007, **46**, 4956–4959.
21 R. Kandre and A. D. Schlüter, *Macromol. Rapid Commun.*, 2008, **29**, 1661–1665.
22 S. Mathew, L. A. Crandall, C. J. Ziegler and C. S. Hartley, *J. Am. Chem. Soc.*, 2014, **136**, 16666–16675.
23 G. Wegner, *Macromol. Symp.*, 2003, **201**, 1–10.
24 M. Ballauff, *Angew. Chemie Int. Ed.*, 1989, **28**, 253–267.
25 S. Jakob, A. Moreno, X. Zhang, L. Bertschi, P. Smith, A. D. Schlüter and J. Sakamoto, *Macromolecules*, 2010, **43**, 7916–7918.
26 H. Diliën, J. Vandenbergh, F. Banishoeb, P. Adriaensens, T. J. Cleij, L. Lutsen and D. J. M. Vanderzande, *Macromolecules*, 2011, **44**, 711–718.
27 R. R. Søndergaard, K. Norrman and F. C. Krebs, *J. Polym. Sci. Part A Polym. Chem.*, 2012, **50**, 1127–1132.
28 E. Bundgaard, O. Hagemann, M. Bjerring, N. C. Nielsen, J. W. Andreasen, B. Andreasen and F. C. Krebs, *Macromolecules*, 2012, **45**, 3644–3646.

29 A. R. Postema, K. Liou, F. Wudl and P. Smith, *Macromolecules*, 1990, **23**, 1842–1845.
30 C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669–2676.
31 J. Li, H. Fu, P. Hu, Z. Zhang, X. Li and Y. Cheng, *Chemistry*, 2012, **18**, 13941–13944.
32 R.-D. Rusu and A. D. Schlüter, *RSC Adv.*, 2014, **4**, 57026–57034.
33 J. Sakamoto, M. Rehahn and D. Schlüter, in *Design and Synthesis of Conjugated Polymers*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 45–90.
34 A. D. Schlüter, *J. Polym. Sci. Part A Polym. Chem.*, 2001, **39**, 1533–1556.
35 S. P. Jakob, ETH Zürich, 2013.
36 H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, 1950, **18**, 1600–1606.
37 B. Hohl, L. Bertschi, X. Zhang, A. D. Schlüter and J. Sakamoto, *Macromolecules*, 2012, **45**, 5418–5426.
38 H. G. Kuivila, J. F. Reuwer Jr. and J. A. Mangravite, *Can. J. Chem.*, 1963, **41**, 3081–3090.
39 L. Metzler, T. Reichenbach, O. Brügner, H. Kober, F. Lombeck, S. Müllers, R. Hanselmann, H. Hillebrecht, M. Walter and M. Sommer, *Polym. Chem.*, 2015, **6**, 3694–3707.
40 H. Komber, S. Müllers, F. Lombeck, A. Held, M. Walter and M. Sommer, *Polym. Chem.*, 2014, **5**, 443–453.
41 S. Vanhee, R. Rulkens, U. Lehmann, C. Rosenauer, M. Schulze, W. Köhler and G. Wegner, *Macromolecules*, 1996, **29**, 5136–5142.
42 H. Yu, A. D. Schlüter and B. Zhang, *Macromolecules*, 2014, **47**, 4127–4135.



A high molar mass poly(*m*,*p*-phenylene) with acid cleavable side chains was synthesised. Further the material was processed into films and subjected to a cleaving procedure yielding insoluble films of unsubstituted polyphenylene.
73x39mm (300 x 300 DPI)