7916 *Macromolecules* **2010**, *43*, 7916–7918
DOI: 10.1021/ma101771t

Macromolecules
COMMUNICATION TO THE EDITOR

Synthesis of Polyphenylenes from a Soluble Precursor: The "Shaving" Approach

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Received August 3, 2010
Revised Manuscript Received August 26, 2010

Polyphenylenes and related aromatic polymers are of increasing importance because of their physical and chemical properties, which are attractive for various applications.[1] Despite this potential, it is often the poor solubility of these polymers that is a critical issue—not only in terms of characterization and processing but also even for synthesis.[2] If no measures are taken to increase their solubility, growing polymer chains precipitate out at an early stage and further increase in length comes to a halt.

It is well-known that the solubility of many conformationally hindered, rigid rod-type polymers can be increased considerably by the attachment of flexible side chains ("hairy-rod" concept).[3] The attachment of such side chains, however, not only "dilutes" backbone properties, but can alter them in various directions.[4] It has therefore always been of interest to be able to remove the solubilizing side chains in order to exploit the intrinsic backbone properties.[5] The present paper describes the synthesis of trialkylsilyl-based hairy-rod-type derivative of a poly(*m*,*p*-phenylene) having a considerable molar mass by using Suzuki polycondensation (SPC).[6] These groups on aromatics are known to be removable by protodesilylation chemistry.[7] The synthesis is then followed by "shaving" the hairs off in order to obtain the parent polyphenylene (Figure 1). Note that other precursor approaches were previously reported for instance by Feast et al.[8] and Ballard et al.[9] However, these approaches generally are limited to selected polymers, such as polyacetylene and poly(*p*-phenylene), respectively. In the latter case, there is also a drawback which is heterogeneity of the product structures.[10,11] The main advantages of the present "shaving" approach in comparison to the other precursor routes are the structurally fully defined precursor with chemical and thermal stabilities and the potential applicability to a broad range of aromatic polymers.

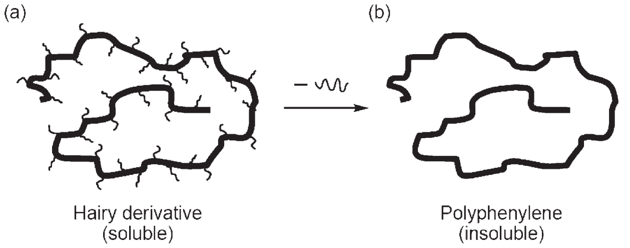
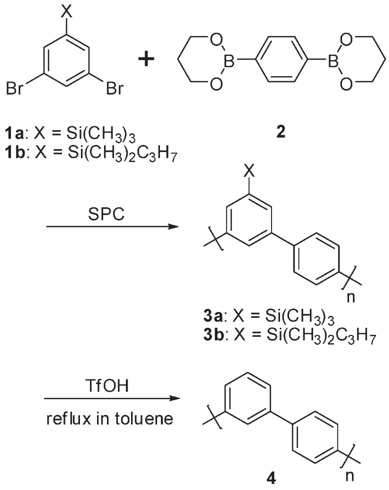


Figure 1. Illustration of the "shaving" process which converts a soluble and, thus, characterizable precursor polymer into its insoluble analogue.

Scheme 1. SPC Synthesis of the Precursor Polymers 3 with Monomers 1 and 2, Followed by Desilylation of 3 To Yield the Parent Polyphenylene 4



From a viewpoint of atom efficiency, trimethylsilyl (TMS) was the first choice as solubilizing group. It was attached to the corresponding monomer **1a** using TMS chloride via monolithiation of 1,3,5-tribromobenzene[12] (Scheme 1). The monomer was purified by recrystallization and subjected to SPC with a 1,4-phenylenediboronate **2** under previously reported conditions,[13] aiming at preparation of the corresponding hairy polymer **3a**. However, these products precipitated out from solution during the polymerization, and also turned out to be hardly soluble in any common solvent after recovery. Obviously, TMS did not mediate sufficient solubility. We, therefore, employed the dimethylpropylsilyl (DMPS) group instead. Synthesis of the corresponding monomer, **1b**, was performed in analogy to **1a**. Silica-gel chromatography of the product mixture afforded a fraction which contained the desired monomer and starting material only, from which the latter was subsequently distilled off to furnish **1b** on a 10 g scale. The purity of **1b** was estimated NMR spectroscopically to be ca. 99.5% by using a ^{13}C-satellite as a reference (Figure S3 in the Supporting Information).[13]

New SPC of **1b** with **2** was conducted under the above conditions (**1b**, 2.543 g; **2**, 1.860 g). While the polymeric products still partially precipitated out during the reaction, after isolation they were found to be largely soluble in chloroform at room temperature. Polymer **3b** was obtained in near quantitative yield after washing the solution with aq. NaCN and subsequent precipitation into methanol. The molecular weight of **3b** were determined to be M_w = 65 700 (P_w = 260) and M_n = 19 500 (P_n = 77) by GPC analysis based on universal calibration.[14,15] Structural integrity of the obtained polymer **3b** was proven by solution ^{1}H and ^{13}C NMR spectroscopy (Figure 2). The products were also analyzed by MALDI−TOF mass spectrometry (Figure S5 in the Supporting Information). Unfortunately, peak assignment of MALDI−TOF mass spectra is rarely straightforward for SPC products[16] because of the different end group patterns possible. Consequently, for each chain with a particular number of repeat units, rather complex signal patterns can be obtained. These patterns may be further complicated by reactions during the laser

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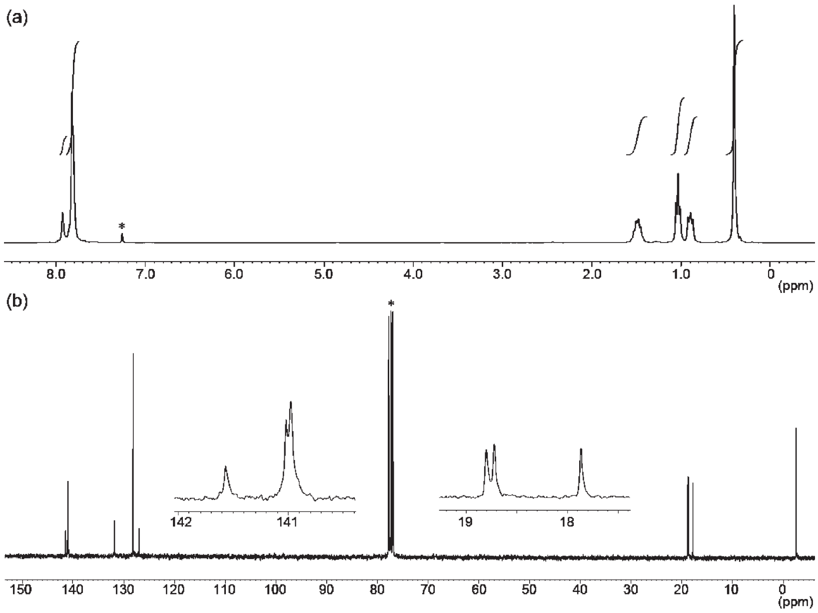

Figure 2. ^{1}H (a) and ^{13}C NMR spectra (b) of the hairy polyphenylene **3b** in chloroform-*d*. The solvent signals are marked (∗).

desorption/ionization process. This holds true for the present case as well. Nevertheless, the major series of the detected peaks distributed equidistantly by the interval of 252 Da, which corresponds to the mass of the repeat unit (M_1M_2,) of the expected sequence of **3b** (Note that M_1 and M_2 represent the moieties resulting from monomers **1b** and **2**, respectively). Additional peaks were detected which are either 176 or 76 Da higher, corresponding to $(M_1M_2)_nM_1$ and $M_2(M_1M_2)_n$, respectively. These additional peaks are important, because their existence unequivocally proves that polymer **3b** cannot consist of cyclic structures only, but must contain open, linear ones as well (see below).

Next, the soluble precursor **3b** was subjected to desilylation in order to remove the side chains. First tributylammonium fluoride (TBAF) was selected, but no desilylation was observed under the conditions employed (1 week reflux in THF with TBAF•H_2O, 1 equiv per DMPS). By contrast, white products precipitated out when toluene solutions of **3b** were refluxed with trifluoromethanesulfonic acid (TfOH, 10 equiv per DMPS) for 1 d. After workup with aqueous base, the insoluble products were collected by filtration, washed by Soxhlet extraction sequentially with isopropyl alcohol, hexane, and diethyl ether and then dried in vacuo. After this procedure, polymer **4** (Scheme 1) was isolated as a fine powder in a yield of 61%. The losses of almost 40% of the mass are due to complications with recovery of the insoluble products from the reaction vessel and the filters.

The disappearance of the silyl groups was confirmed by solid-state MAS ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR (Figure 3) spectroscopy, as well as IR spectroscopy (Figure S6 in the Supporting Information). Thus, the desilylation was virtually quantitative. Additionally, no signal was observed in the solid-state ^{19}F NMR spectrum of **4**, indicating that the desilylating reagent was neither integrated in the polymer structure, nor remained as residual impurity (Figure S7 in the Supporting Information).

Polymer **4** was also subjected to combustion analysis. The obtained results (C, 93.58; H, 5.40 (%)) are in sufficient agreement with the calculated values (C, 94.70; H, 5.30 (%)), which are solely based on repeat units; the nature of the end groups in **4** remains unclear. It should be noted that the polymerization presented involves a kinked monomer, which should increase the probability of cycle formation.[17] In this context, attention is drawn to the GPC-elution curve of the raw precursor polymer **3b** (Figure S4 in the Supporting Information). It was not fully monomodal but rather featured a shoulder at higher retention times and, thus, at lower molar masses. Solvent-free MALDI−TOF

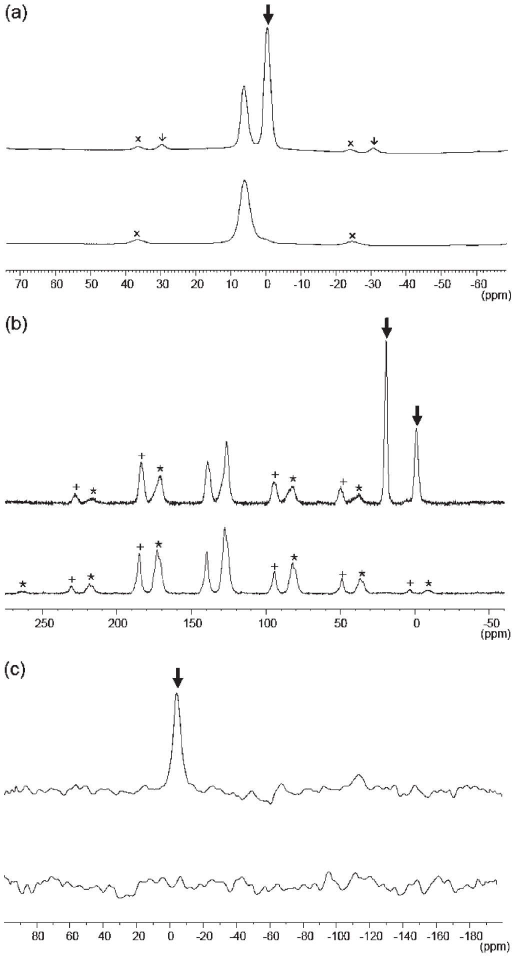

Figure 3. Solid-state MAS ^{1}H NMR (a), ^{13}C NMR (b), and ^{29}Si NMR (c) spectra of the hairy precursor **3b** (upper) and the insoluble product **4** after the desilylation (lower). The signals attributed to the dimethylpropylsilyl groups of **3b** are indicated by arrows. Spinning sidebands are marked (↓, ×, ★, and +).

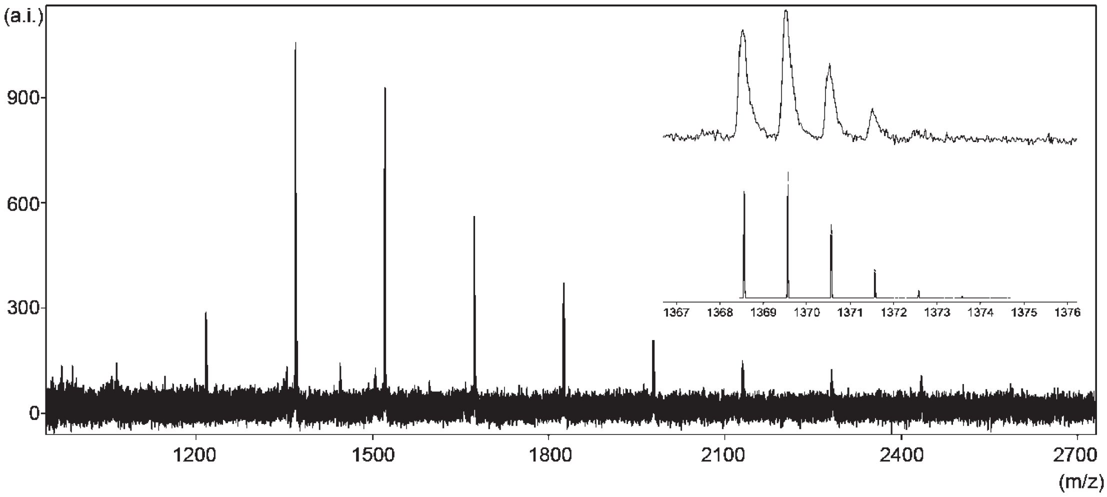

Figure 4. MALDI−TOF mass spectra recorded for the insoluble products **4** (matrix: tetracyanoquinodimethane (TCNQ)). The detected molecular weight values fully match those of cyclic polyphenenyles. Monoisotopic masses: calcd for $(C_{12}H_8)_n$ $[(M_1M_2)_n]^+$, 1064.44 (n = 7), 1216.50 (n = 8), 1368.56 (n = 9), 1520.63 (n = 10), 1672.69 (n = 11), 1824.75 (n = 12), 1976.81 (n = 13), 2128.88 (n = 14), 2280.94 (n = 15), 2433.00 (n = 16); found, 1064.38, 1216.44, 1368.53, 1520.58, 1672.62, 1824.62, 1976.74, 2128.88, 2280.89, 2432.85. The inset shows a magnified part of the spectrum (upper), in good agreement with the simulated isotope pattern of $(C_{12}H_8)_9$ (lower).

mass analysis[18] of **4** provided a firm evidence for the presence of these cycles (Figure 4). The series of molecular weight values detected exactly matches those of *cyclic* polyphenylenes. Note that neither partially "shaved" products nor any open, linear polyphenylnes were detected. While the latter was expected from the convincing structural analyses aforementioned, the lack of any signature of *linear* polyphenylenes is corroborated by the fact that the MALDI−TOF mass spectrum does not show any signals due to $(M_1M_2)_nM_1$ and $M_2(M_1M_2)_n$, which were prominently present in the precursor polymer. Obviously "shaving" hindered individual chains with open, linear structures from desorption/ionization, which might be attributed to enhanced intermolecular interactions among them in the bulk polymer.

As a next step, the present promising approach will be applied for the synthesis of various other polyarylenes, including poly(*p*-phenylene). In addition, the soluble hairy precursors will be processed into desired shapes (e.g., film or fiber) and, thereafter, be converted into the parent materials, for which the reaction conditions still need to be optimized.[19]

Acknowledgment. The authors thank Dr. T. Schweizer (ETHZ) for help in GPC analyses and Prof. B. T. King (University of Nevada, Reno) for useful comments particularly on infrared and combustion analyses of the products. This work was financially supported by the Swiss National Science Foundation (200020-126451).

Supporting Information Available: Text giving all experimental procedures including figures showing NMR and HR−MS data of **1b**, GLC-elusion curve and MALDI−TOF mass spectrum of **3b**, infrared spectra of **3b** and **4**, and solid-state MAS ^{19}F NMR spectrum after "shaving". This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See the following reviews, for example: (a) Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653. (b) List, E.; Jachim, W.; Scherf, U. in *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; CRC Press LLC: Boca Raton, FL, 2007, Vol. *1*, pp 5/1−5/35.(c) Grimsdale, A. C.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5592.

(2) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361.

(3) For example, see: Wegner, G. *Macromol. Chem. Phys.* **2003**, *204*, 347.

(4) For example, see: Postema, A. R.; Liou, K.; Wudl, F.; Smith, P. *Macromolecules* **1990**, *23*, 1842.

(5) Rehahn, M.; Schlüter, A. D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

(6) For initial syntheses of soluble poly(*p*-phenylene) derivatives by SPC, see: Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060.

(7) For example, see: (a) Chan, T. H.; Felming, I. *Synthesis* **1979**, 761. (b) Eaborn, C. *Pure Appl. Chem.* **1969**, 375.

(8) For example, see the following review describing the "Durham route" to polyacetylene: Feast, W. J.; Friend, R. H. *J. Mater. Sci.* **1990**, *25*, 3796.

(9) (a) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *Macromolecules* **1988**, *21*, 294. (b) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *J. Chem. Soc. Chem. Commun.* **1983**, 954.

(10) For discussion on this issue, see: McKean, D. R.; Stille, J. K. *Macromolecules* **1987**, *20*, 1787 and ref 8 .

(11) For improvement of the Ballard approach, see: (a) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10934. (b) Gin, D. L.; Conticello, V. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10507.

(12) Lin, C.-H.; Tour, J. *J. Org. Chem.* **2002**, *67*, 7761.

(13) Kandre, R.; Feldman, K.; Meijer, H. E. H.; Smith, P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 4956.

(14) The universal calibration was obtained with an online viscometer. For the principle, see: Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.

(15) The conventional method relative to retention times of polystyrene standards was also applied to the present case. The obtained values were M_w = 30 and M_n = 8 kg/mol, which were underestimated in comparison to those from the universal calibration. Note that, for poly(*p*-phenylene)s, it is known that this conventional method tends to overestimate the molar mass. For details, see: Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Köhler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136.

(16) For a few cases of successful peak assignments, see: (a) Sangvikar, Y.; Fischer, K.; Schmidt, M.; Schlüter, A. D.; Sakamoto, J. *Org. Lett.* **2009**, *11*, 4112. (b) Jayakannan, M.; van Dongen, J. L. J.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 5386.

(17) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 251.

(18) Trimpin, S.; Rouhanipour, A.; Az, R.; Räder, H. J.; Müllen, K. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1364.

(19) For a related study, see: Naidu, B. V. K.; Jin, S.-H.; Kim, S.-C.; Shin, W.-S.; Lee, J. W.; Gal, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6498. This paper refers to desilylation on a film of poly[2-(3-dimethyldodecylsilylphenyl)-1,4-phenylenevinylene]. The desilylation was assumed to be completed by dipping the film in a 1:1 mixture of trifluoroacetic acid/hexane at ambient temperature for 24 h. However, no experimental data is provided in order to inspect the degree of desilylation.